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KINETICS OF PARTICLE GROWTH
IN A
FLUIDIZED CALCINER

by
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ABSTRACT

Fluidized calcination involves the injection of an atomized feed solution containing dissolved solids into a bed of fluidized particles at elevated temperatures suitable for drying and calcining. As a tremendous quantity of radioactive waste liquor from nuclear fuel reprocessing is at present stored at great cost, this process is most promising as a means to convert such waste liquor to a granular solid form for ultimate disposal. The control of the size of particles in a fluidized calciner is essential for the stability of its operation. The purpose of this investigation was to study the factors underlying the mechanisms of particle growth.

The study was conducted in a three-inch diameter fluidized column using aluminum oxide as bed material and aqueous aluminum nitrate solution as feed. Products were removed at regular intervals to maintain a constant bed weight. Particle growth was traced by adding radioactive aluminum oxide seeds of a given size to the starting bed and following their progress as they grew into successively larger sieve fractions. The effects on the growth rate of operating variables and physical properties of the feed were studied, including fluidizing air velocity, atomizing air rate, column temperature, feed concentration, feed rate, and viscosity and surface tension of the feed.

For each product using screen analysis and gamma-counting data a volume-surface mean diameter of the seed-containing particles was calculated. Upon statistical analysis a linear relationship between the mean diameter of seed-containing particles and time exhibited very strong correlation, substantiating the hypothesis that particle growth was proportional to its surface area. From this linear relationship

the overall growth constant, equal to the slope, was obtained. Attrition effect of the atomizing air was found statistically to be non-significant. Normal growth far outweighed attrition and for steady-state operation other methods to produce seeds, such as jet or target attrition must be employed to balance normal growth. After isolating a number of factors through theoretical considerations, the remaining variables controlling normal growth were closely correlated with the normal growth coefficient through the following equation:

$$K = \frac{9.83 \times 10^3 \left(\frac{F}{W}\right)^{1.25} B^{-0.467} V^{-0.147} \mu^{0.0628} \sigma^{-0.321} V_s' (1 - \epsilon)}{bW}$$

$$\left[1 - \frac{\rho_s (1 - \epsilon)}{\rho_{bs}} \right]$$

A scale-up factor was obtained through comparison with the results from other investigations conducted in larger columns. An equation for predicting steady-state particle-size distribution was found to be applicable if jet or target attrition data were available.

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LIST OF NOMENCLATURE

Symbol	Dimensions
<u>Roman Letters</u>	
A_c Column Cross-Sectional Area	ft^2
A Activity of Particles	counts/min/gm
a Overall Growth Constant	inch/hr
B Ratio of Atomizing Air Rate to Feed Rate	dimensionless
b Volume Shape Factor	dimensionless
C Attrition Coefficient	lb/hr.ft^2
D Diameter of a Particle	ft
D_c Diameter of Column	inch
D_p Average Diameter of Particles in a Fluidized Bed	ft
D_{vs} Volume-Surface Mean Diameter of Particles	inch
d_{vs} Volume-Surface Mean Diameter of Particles	mm.
d Differential Operator	
F Solids Feed Rate	gm/hr
f Friction Factor	dimensionless
G Mass Velocity of Fluidizing Air	lb/hr.ft^2
g_c Gravitational Constant	$\text{ft-lb/lb(force)hr}^2$
j_d Mass-Transfer Factor	dimensionless
K Normal Growth Coefficient	lb/hr.ft^2
K' Equal to kk_1k_2	
k Proportionality Constant	lb/hr.ft^2
k_1 Proportionality Constant	dimensionless
k_2 Proportionality Constant	dimensionless
L_F Fluidized Bed Height	ft
L_s Static Bed Height	ft

LIST OF NOMENCLATURE
(Continued)

Symbol		Dimensions
<u>Roman Letters</u>		
L_o	Fictitious Bed Height with no Voids	ft
M	Mass	lb
m	Mass of a Single Particle	lb
N	Number of Particles	
N_s	Number of Particles in the Spray Zone	
N_t	Number of Particles in the Entire Bed	
n	Number of Observations	
n'	State-of-Flow Factor	dimensionless
ΔP	Pressure Drop across Fluidized Bed	lb/ft ²
Q	Equal to $6(\sigma/\alpha)^3 + 6(\sigma/\alpha)^2 + 3(\sigma/\alpha)$	dimensionless
R_c	Column Radius	ft
Re'	Modified Reynolds Number	dimensionless
r	Correlation Coefficient	dimensionless
s_e^2	Variance of Estimate	
s_p^2	Estimated Population Variance	
T	Temperature	°C
V	Fluidizing Linear Velocity	ft/sec
V'_s	Volume of Spray Cone in Empty Column	ft ³
V_s	Volume of Spray Cone	ft ³
V_T	Volume of Fluidized Bed	ft ³
W	Weight of Fluidized Bed	lb
$\bar{W}$	Weight of a Sample	gm
W_{SB}	Weight of Seed-Containing Particles	gm
W_{So}	Initial Weight of Seeds	gm

LIST OF NOMENCLATURE
(Continued)

Symbol		Dimensions
<u>Roman Letters</u>		
w	Weight of a Sieve Fraction	gm
X	Any Variable	
<u>Greek Letters</u>		
α'	Ratio of Weight Rate of Product Withdrawal to the Total Weight of Bed	hr ⁻¹
α	Exponent	dimensionless
β	Exponent	dimensionless
γ	Exponent	dimensionless
δ	Exponent	dimensionless
ϵ	Bed Voidage Fraction	dimensionless
θ	Angle	radian
θ_F	Residence Time in Fluidized Bed	hr
θ_S	Residence Time in Spray Zone	hr
λ, λ'	Constants	
μ	Viscosity of Feed	lb/hr.ft
μ_F	Viscosity of Fluidizing Air	lb/hr.ft
ν	Constant	
ρ_s	Solids Density	lb/ft ³
ρ_{bs}	Bulk Density of Static Bed	gm/cc
ρ_{bF}	Bulk Density of Fluidized Bed	gm/cc
σ	Surface Tension of Feed	dynes/cm
σ'	Equal to a/D_o	hr ⁻¹
τ	Exponent	dimensionless
ϕ_s	Surface Shape Factor	dimensionless
ϕ	Constant	
ω	Exponent	dimensionless

I. INTRODUCTION

Definition of Problem, Choice of System, and Scope of Investigation

Fluidized calcination is a process that incorporates the features of spray drying and fluidization. A feed solution containing dissolved solids is atomized by a spray nozzle and injected into a fluidized column operating at elevated temperatures and is subsequently dried and calcined, producing solid particles which are continuously withdrawn as product. This process offers the advantage of continuous operation, good heat transfer characteristics, and uniform bed temperature. Moreover, since this process can be easily controlled remotely and involves no moving parts that require seals or packings, it is readily adaptable for use in the nuclear energy field where radioactivity in the material to be processed makes these features most desirable.

In the nuclear energy field, fluidized calcination finds application in two areas, namely, in the thermal decomposition to uranium trioxide of uranyl nitrate from an intermediate step in the processing of uranium metal from ores or reprocessed nuclear fuels, and in the conversion from liquid to solid form of wastes from the reprocessing of nuclear fuels for ultimate disposal⁽³⁰⁾. With regard to the production of uranium trioxide from uranyl nitrate, a continuous process is sought to replace the batch operation now in use⁽³⁷⁾. In the case of waste disposal, no established method has been found and the waste liquor is now stored in large underground tanks⁽⁶⁵⁾. Due to the fact that work with radioactive material necessarily involves extensive precautionary measures and added equipment for health protection, the system chosen for the present study is an aqueous aluminum nitrate solution similar to the waste liquor but without activity.

The problem of satisfactory waste disposal can be properly appreciated when it is realized that most of the fissionable material in a nuclear fuel element removed from a reactor after undergoing the allowable burn-up is still un-used and must be recovered from economic considerations. In the recovery steps tremendous quantities of aluminum nitrate waste solution containing fission products are produced. The aluminum nitrate comes from the fuel elements themselves and/or from the separation steps of fissionable and non-fissionable materials. Because of the obvious hazards involved, these wastes cannot be disposed of in the conventional manner. Aluminum nitrate type waste now stored is on the order of 10 million gallons and this figure mounts with each day⁽⁵⁵⁾. It is clear then that adequate means must be provided to handle this situation. Of the various processes proposed, fluidized calcination stands as the most promising. In the fluidized calcination of aluminum nitrate, a volume reduction of six or eight to one⁽³⁰⁾ has been achieved. Furthermore, the process converts the waste from a liquid to a granular solid which is much more easily handled for ultimate disposal. A 2-ft. square calciner has been constructed at the Idaho Chemical Processing Plant and is now operating⁽²²⁾.

In a fluidized column the control of the size of particles is of prime importance for the stability of its operation. Hence, the factors that influence changes in particle size must be determined before this process can be successful. However, when one considers that the factors operative in fluidization and spray drying are themselves far from understood, it becomes apparent that fluidized calcination, which combines these two unit operations, would be exceedingly difficult to analyze. This study is initiated to investigate some of the factors involved and to bring the situation a step closer to its eventual complete analysis.

The overall change in particle size may be considered the result of the combined interaction of the following mechanisms. 1) Normal growth due to the continuous addition of feed, and 2) agglomeration of smaller particles to form larger ones tend to increase the average particle size. On the other hand, 3) attrition due to particle collisions and the action of atomizing gas and 4) possible new nuclei formation from the evaporation of fine spray droplets tend to decrease the average particle size. In addition 5) chemical reaction may also affect the size of particles. Each of these mechanisms is related in a complex manner to the physical properties of the system and the operating variables of the unit. The combined interaction of all these mechanisms multiplies the degree of complexity. Thus, in order to define a reasonable scope for this investigation, the major factors contributing to particle size change, the mechanisms of normal growth and attrition are studied with some consideration for chemical reaction.

Previous Work and Background

Fluidized calcination work has been carried out at the Argonne National Laboratory^(29, 30, 38, 39), the Idaho Chemical Processing Plant^(21,22), and the Mallinckrodt Chemical Works^(11,57,58). Work at Argonne included both calcination of uranyl nitrate and aluminum nitrate solutions, while Idaho and Mallinckrodt have been engaging in the calcination of aluminum nitrate and uranyl nitrate solutions, respectively. The aim of these investigations was to obtain combinations of operating variables that would ensure satisfactory continuous operation of the calcination unit. From these efforts, it became clear that the rate of feeding, the solids content in the feed, the nozzle atomizing air flow rate, the fluidizing air flow rate, and the temperature of the fluidized bed were factors that affected particle growth. The present project is mainly concerned with the study of these variables

along with some physical properties of the feed solution.

Uranyl nitrate solution from ore processing or from fuel reprocessing was thermally decomposed in a calciner and granular uranium trioxide meeting the requirements of chemical composition was produced^(11,30,57,58).

Aluminum nitrate solution of the same chemical composition as the actual waste liquor but diluted in activity was processed at Argonne^(38,39) in a 6-inch diameter pilot-plant calciner, producing solid granular aluminum oxide satisfactory for subsequent disposal. This field is continuing at the Idaho plant where a 2-ft square calciner unit is under operation. A program for studying particle growth was reported⁽²²⁾ in August 1959 but very little of the results was available. Results from the present study are discussed in conjunction with these in the Discussion section.

From the work at Argonne it was found that the arrangement and location of the spray nozzle relative to the fluidized bed were critical. For example, the location of the nozzle above the bed with the spray directed onto the surface of the fluid bed resulted in caking both in the bed and on the nozzle. Likewise, mounting the nozzle through a hole in the gas distributing plate at the bottom of the bed with the spray directed upward also resulted in caking around the nozzle⁽³⁰⁾. After several arrangements had been tried, it was found that mounting the atomizing nozzle horizontally through a hole in the side of the fluidized bed section and spraying the feed into the bed perpendicular to the axis of the bed section resulted in satisfactory operation.

Other than the above work, very little information is available in the literature to guide this study as fluidized calcination is still a relatively new technique. Except for the paper by Griffin, et al⁽²⁰⁾ dealing with the Esso Fluid Coking Process, there seems to be no other reported commercial use of a fluidized calciner. However, details of

the Esso process have not been disclosed. Hence, a literature search was undertaken for possible leads to the correct mechanisms of particle growth. The survey was not intended to be exhaustive, but was concentrated toward the more recent concepts and development.

Griffin, et al.⁽²⁰⁾ described particle size control in fluid coking, a process quite similar to the one investigated here. Mathematical models were given for both selective and non-selective withdrawal of the steady-state mixture, and equations were derived for the steady-state particle distribution. No consideration was given to the agglomeration of particles.

A number of articles dealt with particle size variation in spray drops. Duffie and Marshall⁽¹²⁾ studied evaporation from pure liquid droplets but did not arrive at any quantitative conclusion with droplets containing dissolved solids. Meyer⁽⁴⁵⁾ made a study of factors affecting particle size at high feed rates and atomizer peripheral speed approaching commercial scale but found no clear cut correlation. Wallman and Blyth⁽⁶³⁾ investigated the particle size and distribution of sodium silicate in a Bowen-type spray dryer and noted that particle size changed directly with feed rate and feed solids concentrations, inversely with atomizer speed and diameter, and very little change with feed viscosity, feed temperature, and drying gas velocity. The results of other studies on spray-drying, drying, and fluidization reported in the literature are discussed in the Appendix.

II. ANALYSIS OF PARTICLE GROWTH

As mentioned in the previous section, normal growth and attrition are the factors of prime interest in this investigation. The normal growth aspect of the problem is analyzed first.

Consider a particle of diameter D . This particle only picks up feed when passing through the zone formed by the spray droplets. If it is assumed that the rate of growth in the spray zone is proportional to the surface area of the particle, then the mass growth rate can be expressed as

$$\frac{dm}{d\theta_s} = kD^2 \quad (1)$$

where m = mass of the particle
 D = diameter of the particle
 θ_s = residence time in the spray zone
 k = proportionality constant

This assumption is supported by the general observation that particles from the fluidized dryer-calciner grow by adding concentric layers of solids of uniform thickness.

In equation (1), however, since the residence time in the spray zone is not a readily measurable quantity, it is converted to the total residence time of the particle in the bed, θ_F , through the following relationship:

$$\frac{d\theta_s}{d\theta_F} = \frac{N_s}{N_T} \quad (2)$$

where N_s = number of particles in the spray zone

N_T = number of particles in the entire bed.

Then, equation (1) becomes

$$\frac{dm}{d\Theta_F} = k \frac{N_S}{N_T} D^2 \quad (3)$$

Further, $\frac{N_S}{N_T}$ is replaced by $k_1 \frac{V_S}{V_T}$, where V_S = volume of the spray

zone, V_T = volume of the entire fluidized bed, and k_1 is the factor that accounts for deviations from uniformity in bed density in the spray zone due to the injection of feed and the atomizing air, k_1 being unity when the bed density is uniform. So equation (3) becomes

$$\frac{dm}{d\Theta_F} = k k_1 \frac{V_S}{V_T} D^2 \quad (4)$$

But in a continuous operation under steady state $\frac{V_S}{V_T}$ is a constant.

Now let $k k_1 \frac{V_S}{V_T} = K$, and write equation (4) as

$$\frac{dm}{d\Theta_F} = K D^2 \quad (5)$$

defining K as the normal growth coefficient.

In analyzing the factors affecting K , fundamental concepts are considered first. When such analysis cannot be carried further, a coefficient then incorporates the effects of all the factors not accounted for by theoretical considerations. With this goal in mind, recall that

$$K = k k_1 \frac{V_S}{V_T}$$

Now V_S can be considered as

$$V_S = k_2 \left(\frac{\rho_{bs} - \rho_{bF}}{\rho_{bs}} \right) V'_S$$

where V'_s = volume of spray zone if the column were empty (see Appendix for mathematical derivation for a conical spray),

ρ_{bs}, ρ_{bF} = bulk density of the static and fluidized bed, respectively,

k_2 = factor that accounts for the distortion of the spray zone by the fluidized solids.

The fluidized bed volume, V_T , equals the cross-sectional area A_c of the column times the fluidized bed height L_F . Thus

$$K = k k_1 \frac{V_s}{V_T} = k k_1 k_2 \left(\frac{\rho_{bs} - \rho_{bF}}{\rho_{bs}} \right) \frac{V'_s}{L_F A_c}$$

Moreover, let W be the bed weight, then

$$\rho_{bs} = \frac{W}{L_s A_c}$$

and

$$\rho_{bF} = \frac{W}{L_F A_c}$$

where L_s is the static bed height. Substituting these values, there results

$$K = k k_1 k_2 \frac{V'_s}{L_F} \left(1 - \frac{L_s}{L_F} \right) \quad (6)$$

The fluidized bed height, L_F , may be correlated in terms of the bed external voidage fraction, ϵ , as follows:

$$\epsilon = 1 - \frac{L_o}{L_F} \quad (7)$$

where L_o = fictitious bed height when no external voidage is present

$$= \frac{W}{\rho_s A_c}$$

ρ_s = solids density.

Then

$$L_F = \frac{L_o}{1-\epsilon} = \frac{W}{\rho_s A_c (1-\epsilon)}$$

and

$$L_s = \frac{W}{\rho_{bs} A_c}$$

Substituting for these values in equation (6),

$$K = \frac{k k_1 k_2 V'_s \rho_s (1-\epsilon)}{W} \left(1 - \left[\frac{\rho_s (1-\epsilon)}{\rho_{bs}} \right] \right) \quad (8)$$

In this equation V'_s , W , ρ_s , and ρ_{bs} are either measurable or directly calculable. Only the factor ϵ is not easily obtained, especially in a metallic column where the fluidized bed height is not observable. Thus it is calculated through existing correlations.

The Carman-Kozeny equation for pressure drop in fixed granular beds can be extended to fluidized systems by correlating the friction factor with a modified Reynolds Number. The Carman-Kozeny equation as modified by Leva, et al.⁽³⁶⁾ is

$$\Delta P = \frac{2fg^2 L_F (1-\epsilon)^{3-n'}}{D_p \phi^{3-n'} g_c \rho_F \epsilon^3} \quad (9)$$

The state-of-flow factor, n' , equals unity in the laminar region and two in the turbulent region. Chu, et al.⁽⁸⁾ found that the turbulent region was reached at a modified Reynolds Number

$$Re' = \frac{D_p G}{\mu_F (1-\epsilon)}$$

greater than 30. Thus in this region $n' = 2$ and equation (9) can be written as:

$$f = \frac{D_p \Delta P \rho_F \epsilon^3 \phi_s g_c}{2 L_F G^2 (1 - \epsilon)} \quad (10)$$

In the laminar region, $Re' < 30$, $n' = 1$, and equation (9) reduces to

$$f = \frac{D_p \Delta P \rho_F \epsilon^3 g_c \phi_s^2}{2 L_F G^2 (1 - \epsilon)^2} \quad (11)$$

In the turbulent region, Carman⁽⁶⁾ found that

$$\frac{\Delta P g_c \rho_F \epsilon^3}{L_F G^2 a} = 0.4 \left(\frac{G}{\mu_F a} \right)^{-0.1} \quad (12)$$

where $a = \frac{6(1 - \epsilon)}{\phi_s D_p}$ = specific surface of particles per unit volume of bed.

μ_F = fluidizing medium viscosity in lb mass/hr ft

Rearranging equation (12) and isolating G :

$$G^{1.9} = \frac{\Delta P g_c \rho_F \phi_s^{1.1} D_p^{1.1} \epsilon^3}{2.9 L_F \mu_F^{0.1} (1 - \epsilon)^{1.1}} \quad (13)$$

But in a fluidized bed when wall friction is negligible, the pressure gradient equals approximately the weight gradient, that is,

$$\frac{\Delta P}{L_F} = (1 - \epsilon)(\rho_s - \rho_F) \quad (14)$$

In most solid-gas systems, $\rho_F \ll \rho_s$. Then substituting $\frac{\Delta P}{L_F}$

in equation (13) and solving for G :

$$G = \left[\frac{g_c \rho_F \phi_s^{1.1}}{2.9 \mu_F^{0.1}} \right]^{0.526} D_p^{0.579} \rho_s^{0.526} \frac{\epsilon^{1.58}}{(1 - \epsilon)^{0.0526}} \quad (15)$$

An alternate correlation for turbulent fluidized bed by Chu, et al.⁽⁸⁾ predicts that $f/10 = j_d$, the mass transfer factor, which in turn is correlated by

$$j_d = 1.77 \left[\frac{D_p G}{\mu_F (1-\epsilon)} \right]^{-0.44}$$

Then

$$f = 17.7 \left[\frac{D_p G}{\mu_F (1-\epsilon)} \right]^{-0.44} \quad (16)$$

Equating equations (10) and (16), and again introducing $\Delta P/L_F = (1-\epsilon) \rho_s$, upon solving for G, there results:

$$G = \left(\frac{g_c \rho_F \phi_s}{35.4 \mu_F} \right)^{0.641} \rho_s^{0.641} D_p^{0.923} \frac{\epsilon^{1.923}}{(1-\epsilon)^{0.282}} \quad (17)$$

In the laminar region, Carman⁽⁶⁾ found that

$$\frac{\Delta P g_c \rho_F \epsilon^3}{L_F G^2 a} = 5 \left(\frac{G}{\mu_F a} \right)^{-1}$$

Substituting for $\Delta P/L_F$ and solving for G:

$$G = \left(\frac{\rho_F \phi_s^2 g_c}{180 \mu_F} \right) \rho_s D_p^2 \frac{\epsilon^3}{1-\epsilon} \quad (18)$$

Using Chu's correlation in the laminar region, $Re' < 30$,

$$f = 58 \left[\frac{D_p G}{\mu_F (1-\epsilon)} \right]^{-0.78} \quad (19)$$

Equating equation (19) with equation (11), substituting for $\frac{\Delta P}{L_F}$, and solving for G, the following working equation is the result:

$$G = \left(\frac{\rho_{Fc} \phi_s^2}{116 \mu_F^{0.78}} \right)^{0.082} \rho_s^{0.82} D_p^{1.46} \frac{\epsilon^{2.46}}{(1-\epsilon)^{0.416}} \quad (20)$$

Morse⁽⁴⁸⁾ showed that the Carman-Kozeny equation correlated data well for particulate fluidization but failed to give satisfactory correlation in aggregative fluidization. The correlation by Chu, et al. represented data taken in a fluidized bed over a wide range of Reynolds Number and should be more reliable. It is believed, therefore, that equations (17) and (20) are preferable to equations (15) and (18). Thus, knowing G and the physical properties of the particle, the voidage fraction ϵ can be calculated.

Referring to equation (8), having ϵ and the other measurable or known quantities V'_s , W, ρ_s , ρ_{bs} , the group $kk_1k_2 = K'$ can be determined for each value of K, and K' can be correlated with the operating variables.

Attention should be called to the fact that D_p in equations (9) through (20) is the average diameter of all particles in the bed which remains constant for steady-state operation. This diameter should not be confused with D in equation (5) which is the time-dependent diameter of an individual particle.

Next, the attrition aspect of the overall growth mechanism is considered. Here, as in normal growth, the surface area of a particle is of prime importance. Attrition rate is assumed to be proportional to the surface area available for grinding and crushing,

$$\frac{dm}{d\theta_F} = - CD^2 \quad (21)$$

The negative sign corresponds to a decrease in the mass of a particle. The attrition coefficient C can be determined independently of normal growth by conducting runs where no feed is introduced into the fluidized unit. It is related to particle properties such as shape factor, density, and friability, and operating variables such as fluidizing velocity, atomizing air rate, and column temperature. Attempts have been made by Rittinger⁽⁵⁴⁾, Kick⁽³³⁾, and Bond⁽³⁾ to correlate attrition results by means of the theory of comminution. These theories predict the energy required to crush particles and create new surfaces. However, as pointed out by Rosin⁽⁵⁶⁾, about 99 per cent of the total measured energy consumption in pulverizers is not used in disintegration. Hence, theoretical laws such as Rittinger's, which are concerned with approximately one per cent of the total power consumption, have little physical value. Consequently, the attrition coefficient C is observed under various conditions and correlated with significant variables empirically.

As to the effect of chemical reactions on particle growth in a fluidized calciner, this depends primarily on the intrinsic properties of the system selected for study and is not amenable to generalization. Of the operating variables, only temperature should have a possible influence on chemical reaction.

Referring now to equations (5) and (21), they are combined to yield the net growth equation

$$\frac{dm}{d\theta_F} = (K-C) D^2 \quad (22)$$

Thus the net growth rate $\frac{dm}{d\theta_F}$ may be either positive or negative depending on whether normal growth or attrition predominates. Now let

$$m = b \rho_s D^3$$

where b is the volume shape factor of the particle, being $\pi/6$ for spheres.

Then

$$\frac{dm}{d\Theta_F} = 3b \rho_s D^2 \frac{dD}{d\Theta_F} \quad (23)$$

Substituting equation (23) in equation (22), it follows that

$$\frac{dD}{d\Theta_F} = \frac{(K-C)}{3b \rho_s} \quad (24)$$

which upon integration gives

$$D = D_0 + a \Theta_F \quad (25)$$

where

$$a = \frac{K-C}{3b \rho_s} = \text{overall growth constant}$$

D_0 = initial particle size

The overall growth constant, a , is studied. In growth runs where feed is introduced both K and C are involved, whereas in attrition runs K drops out and only C remains. This completes the analysis of the overall growth mechanism.

Some method of tracing particle growth with time has to be devised. After preliminary work, summarized in the Appendix, it is decided to employ radioactive seed particles that are otherwise identical to the particles in the fluidized bed to follow the growth pattern. By adding a known amount of these radioactive particles of given activity to the starting bed of a run, the growth of these seed particles is followed by taking out product samples at regular time intervals, analyzing them for size distribution, and determining the amount of activity of each size fraction. In this manner, the overall growth constant can be calculated.

It would be interesting, after obtaining the overall growth constant, to compare the cumulative growth of these seed particles with an equation derived by Griffin, et al.⁽²⁰⁾.

$$\frac{W_{SB}}{W_{So}} = 1 + Q - e^{-\alpha' \theta_F} \left\{ \sigma'^3 \theta_F^3 + 3 \left[(\sigma'/\alpha')^3 + \sigma'^2 \right] \theta_F^2 + Q(\alpha' \theta_F + 1) + 1 \right\} \quad (26)$$

where W_{SB} = weight of particles in the product that contain seeds

W_{So} = weight of seed particles added initially

$$Q = 6(\sigma'/\alpha')^3 + 6(\sigma'/\alpha')^2 + 3(\sigma'/\alpha')$$

$$\sigma' = a/D_0$$

a = overall growth constant

D_0 = initial seed particle size

α' = ratio of the weight rate of product withdrawal to the total weight of the bed.

This equation was derived by combining the growth equation (25) with a "wash out" equation of the time-decay type:

$$\frac{dX}{d\theta_F} = -\lambda X$$

where X is the quantity that is present in the system at any time θ_F and

λ is a constant.

A family of curves relating $\frac{W_{SB}}{W_{So}}$ as a function of time at a given value of α' are plotted with σ'/α' as parameter, shown on Figure 1.

Equation (26) holds before steady-state is attained. At steady-state, the particle size distribution is predicted by equation (27):

weight per cent of particles in steady-state mixture having a diameter of D or less

$$\begin{aligned}
 = 100 - & \frac{100}{(1 + Q) \exp \left[\left(\frac{D}{D_0} - 1 \right) / \left(\frac{\sigma'}{\alpha'} \right) \right]} \left[\left(\frac{D}{D_0} - 1 \right)^3 \right. \\
 & \left. + 3 \left(\frac{\sigma'}{\alpha'} + 1 \right) \left(\frac{D}{D_0} - 1 \right)^2 + \frac{Q}{(\sigma'/\alpha')} \left(\frac{D}{D_0} - 1 \right) + 1 + Q \right] \quad (27)
 \end{aligned}$$

Figure 1. Predicted Cumulative Growth of Seed Particles with Time

III. LABORATORY EQUIPMENT, EXPERIMENTAL PROCEDURE, AND DATA COLLECTION

Laboratory Equipment:

The basic equipment used in this investigation was an existing three-inch diameter column previously used for calcination studies. Many modifications and additions were made later. A schematic drawing of the complete unit is presented in Figure 2. A diagram of the electrical connections in the system is shown in Figure 3. Photographs of the calciner unit and some of its components are presented in the Appendix.

The stainless steel column consisted of two sections, a 14-inch high fluidizing section of 3-inch schedule 40 pipe and 31-inch disengagement section made by welding a 22-inch piece of 4-inch schedule 40 pipe through a concentric reducer to a 3-inch piece of 3-inch schedule 40 pipe. These two sections were joined by flanges. The spray nozzle assembly was installed 9 inches from the bottom of the fluidizing section, perpendicular to the axis of the column. Fluidizing air entered the bottom of the fluidizing section through a porous sintered stainless steel distributor plate bolted between the two bottom flanges. The filter and blowback assembly were mounted on the top flange of the disengagement section. A vacuum sampling device was attached one inch from the bottom of the fluidizing section.

Feed solution could be introduced either by direct pumping or by static air pressure in the feed tank. Direct pumping from the feed tank was accomplished by a Sigma "finger" pump. The alternate method was to maintain a constant air pressure above the feed solution in the feed tank and force the feed solution out through a rotameter into the column. Direct pumping offered constant flow rate but suffered from pulsation

Figure 2. Schematic Layout and Auxiliary Equipment for the Three-inch Fluidized Calciner

Figure 3. Wiring Schematic for the Three-inch Fluidized Calciner

between pumping cycles and hence was used only at higher flow rates where surging due to pulsation was not pronounced. The air-pressure method provided smooth flow but required attention in flow control and was therefore used for lower flow rates. The feed tank rested on a Toledo scale for weight readings.

High-pressure air, HPA, (100 psig) from the building supplied the various air requirements of the system through pressure regulators, control valves, and rotameters. Off-gas from the unit went first to a primary stainless steel condenser, then through a pair of glass condensers in parallel, and finally vented to the building exhaust system. All condensers were water-cooled. All off-gas lines were stainless steel for protection against nitric acid in the condensate.

The filter and blowback assembly consisted of two 3-inch Micro-metallic porous stainless steel bayonet filters 18-inch long screwed into the top flange of the disengagement section. The fines accumulated on the filters were returned to the column by the blowback device. High-pressure air entered through a solenoid valve to a steam ejector attached to the off-gas line above each filter. Once every minute each solenoid valve, which was normally closed, was energized and allowed a 1/4-second burst of air through the ejector and down through the filter. These solenoid valves were controlled by an Eagle Multi-Pulse Timer.

Another timer (Sangamo) was connected to the column temperature controller, feed pump, the Multipulse timer, and solenoid valves in the fluidizing and atomizing air lines so that the entire unit could be shut down at any pre-set time. The solenoid valves in the fluidizing and atomizing air lines could be bypassed for manual control.

The stainless steel spray nozzle was a two-fluid pneumatic nozzle type, designed by J. J. Barghusen and D. J. Raue of the Argonne National

Laboratory, based on the Spraying Systems Company's pneumatic nozzle. Feed entered the column through the liquid needle and atomizing air passed through the nozzle housing and the annular opening around the needle into the column where it came into contact with the feed stream. The needle was 0.020-inch ID and 0.048-inch OD and protruded 3/16-inch into the column to eliminate the tendency of lump formation around the nozzle when the tip of the needle was flush with the column wall. The atomizing air port was 0.064-inch in diameter, giving an annular opening of 0.008-inch width. Cooling coils were soldered to the nozzle housing to prevent pre-vaporization of the feed inside the nozzle and thus eliminated solid deposits in the nozzle which caused plugging.

To the 1/4-inch Swagelok fitting on the liquid nozzle was attached a 1/4-inch cross. Water line was connected to one branch and feed line to another. To the third branch a pressure gauge was connected that gave indication of any pressure build-up in the nozzle as a result of plugging. A high-pressure air line was connected to this branch to blow out small deposits in the nozzle.

Sample withdrawal assembly provided high-pressure air to clean out the sample line along with a vacuum pump for drawing vacuum in the Pyrex glass sample bomb. Sample particles were kept out of the vacuum pump by a 1/4-inch stainless steel Hoke in-line micron filter.

The heating of the fluidizing section was supplied by five 1000-watt 220-volt tubular calrod heaters wrapped around the outside of the column. Three of the five calrods were connected to one variac that stayed on all through the run, while the other two were connected to another variac through a Wheelco Temperature Controller for on-off control as indicated by a Chromel-Alumel thermocouple tube inserted in the bed and connected to the controller. An 800-watt, 220-volt Acrawatt band heater provided heat

to the nozzle section since calrods could not be easily wrapped around the nozzle assembly. Heating of the disengagement section and the off-gas line to prevent condensation was accomplished by wrapping them with asbestos-covered Nichrome wire. Nichrome wire was also used to preheat the fluidizing air and the blowback air.

Besides the pressure indicators along the various air lines and the bed thermocouple connected to the temperature controller, pressure drop across the bed was measured by a manometer using Meriam oil #3 (2.95 sp. gr.). Fluidizing air, blowback air, and disengagement section temperatures were indicated by temperature gauges. The bed temperature thermocouple was also connected to a Brown Continuous Temperature Strip Chart Recorder, parallel to the Wheelco Temperature Controller.

Experimental Procedure:

Operation of the fluidization unit consisted of charging the starting bed material into the fluidizing section and then bolting it to the disengagement section through connecting flanges. During the charging process, air was allowed to bleed through the atomizing air annulus and the liquid nozzle to guard against wedging of solid particles in these openings. Next the Sangamo timer was started and heaters, fluidizing air, and blowback air were turned on. When the bed temperature reached the pre-set temperature on the controller, atomizing air was increased to the desired operating rate and water pumped into the column to cool the inside of the nozzle and to acclimate the unit to subsequent feed introduction. When the bed was again up to operating temperature, feeding was started and water cut off. From then on product samples were taken at regular intervals, condensate pot was drained periodically, and feed solution was added as required. When a run was completed, feeding was

stopped and water pumped in for about ten minutes to wash out the nozzle and then the unit was shut down.

The procedure described above was that for runs involving particle growth. Attrition runs were conducted in the same manner except that no nitrate feed was introduced. Instead, water was sprayed into the column to simulate the growth run operating conditions but since it contains no dissolved solids there was no growth, only decrease in particle size due to the attrition action. The attrition runs were of 24-hour duration. After every six hours, the unit was shut down and the entire bed material including the fines on the filters and walls was collected and screened. After screening, the material was put back into the bed and the run continued.

Feed solution was prepared by dissolving reagent grade aluminum nitrate nonahydrate in distilled water to produce the desired concentration. The concentrations listed in the tables are weight per cent of the nonahydrate and not the anhydrous salt.

Starting bed material was obtained by first screening the calciner product aluminum oxide from the Idaho Chemical Processing Plant into various sieve fractions and mixing them in the desired proportions.

Starting beds for all attrition runs and all growth runs except PS-14 were composed of the following fractions:

<u>Mesh Size</u>	<u>Wt %</u>
-20+30	10
-30+40	40
-40+50	38
-50+70	10
-70+100	2

For PS-14, the distribution was slightly different:

<u>Mesh Size</u>	<u>Wt %</u>
-20+30	14
-30+40	46
-40+50	30
-50+70	8
-70+100	2

In all growth runs the -70+100 mesh fractions were tracer seeds, except in PS-52 and PS-53 where 2% of -50+70 mesh seeds was used.

Seeds used as tracers for detecting particle growth were obtained from radioactive calciner product aluminum oxide furnished by J. W. Loeding of the Argonne National Laboratory. The activity was due to ruthenium isotope of one-year half-life, emitting gamma in its disintegration chain. This material was ground and the -100+140 mesh fractions used as seeds directly. However, it was found that upon mixing the "hot" seeds with the other "cold" fractions and fluidizing, the "cold" fractions picked up activity through contact with the "hot" seeds. This resulted in a relatively high "background" gamma count and made calculation of growth rates very difficult because the true picture of growth, detected as the gradual acquisition of activity by successively larger screen fractions, was masked by the high background. Moreover, since not all the fines collected on the bayonet filters could be blown back, leaving a thin layer on the filters, the small seeds tended to be lodged on the filters when the fluidized bed was started.

To remedy this "background" difficulty, it was found that by first coating the "hot" seeds with a layer of inactive aluminum oxide, and then using these coated seeds in the growth study runs, the contact contamination was reduced to satisfactory limits. Thus "seed runs" were made in which original "hot" seeds were coated in a fluidized bed with aluminum nitrate feed for four or five hours; then the bed material was removed and screened, and the -50+70 mesh and -70+100 mesh particles collected as

seeds for growth runs. The seed-coating process reduced the activity of the seeds from 10^6 counts/minute/gram to 10^5 counts/minute/gram, which was still quite adequate for tracing growth.

To overcome the problem of seeds sticking to filters, before each growth run a bed of inactive aluminum oxide was fluidized for five to six hours to coat the filters with a layer of inactive fines so that during growth runs the seeds, when they reached the filter, were blown back into the bed. With these provisions the seed problem was solved.

Growth runs were operated continuously for twenty-four hour periods during which the seeds grew enough so that a good insight into their growth could be gained. The runs were made continuous to eliminate intermediate start-ups and shut-downs. When agglomerates appeared in the products, the run was terminated because agglomeration would tend to foul the activity counts and hence confuse the growth picture.

Product samples were taken from the bed using a vacuum. The sample line was cleaned out by several short bursts of high pressure air and then the vacuum pump drew a vacuum of about 28 inches mercury on the glass sample bomb. A plug valve in the sample line was opened and the desired quantity of product was withdrawn. The entire product-withdrawing step took less than a minute. After each sample, the sample bomb was rinsed with water and dried with acetone to eliminate contamination between samples. Enough product was removed to keep the bed weight constant. At high feed rates, products were taken every half-hour, while with low feed rates, every hour. Each product represented 5% or less of the bed weight so that the entire operation may be considered as constant bed-weight.

Operating variables that were studied in all except two runs consisted of the following: column temperature, fluidizing velocity, atomizing

air rate, feed rate, and feed concentration. Furthermore, the surface tension of the feed solution was reduced in Run PS-60 by a factor of about two through the addition of 0.012 weight per cent of "Tween 20" (an oil made by Atlas Powder Company). In Run PS-61 the viscosity of the feed was increased about five times by adding 0.125 weight per cent of "Natrosol" (one of the cellulose gum products of Hercules Powder Company). Surface tension was determined in a DuNouy["] interfacial tensiometer with platinum-iridium ring. The viscosity was measured in an EXAX K Size 100 viscometer.

Due to the limitations of the equipment, operating variables could not be varied over too wide a range without causing caking in the bed. Unlike the ordinary fluidized bed where operation would not be a major problem, in a fluidized calciner, because of the spraying in of feed, the bed can easily cake when operating variables were changed. High feed rates invariably caused caking. Too much atomizing air caused the spray to penetrate across the bed and deposit solids on the opposite wall, a phenomenon also observed when the bed slugged excessively at high fluidizing velocities. This tendency to cake, inherent in calciner operations, haunted this investigation constantly. A good number of runs ended in failure as a consequence. To obtain the data presented in this work thus constituted a major effort.

Data Collection:

After each run, each product taken during the run was screened into the following fractions: -16+20, -20+30, -30+40, -40+50, -50+70, -70+100, and -100 mesh. The screens were washed with acetone after a few screenings to prevent contamination between samples. Screening was done with a set of 8-inch diameter U. S. Standard Testing Sieves arranged in an order of decreasing screen openings plus a bottom pan and a cover. The sample was

placed on the top or coarsest screen, and the entire stack placed in a Ro-Tap Screening Machine. After ten minutes of screening the machine was stopped. The quantities of particles collected on each sieve were then brushed off the sieves and transferred to separate weighed bottles. These bottles were again weighed to yield the screen analysis of each sample.

The above set of screens was selected according to the accepted practice that the ratio of the length of aperture of a sieve to that of the next finer sieve in the series be $\sqrt{2}$. Thus a definite pattern of a geometric progression was established.

Next, tubes for gamma-counting were tared on an analytical balance and a small quantity of solids transferred to these counting tubes and weighed again. These tubes were then placed in a gamma counter and total counts over a two-minute interval were recorded. From the counts per minute obtained the background counts were subtracted. Then a figure for counts per minute per gram was calculated. For each run between 150 and 200 samples were counted and the entire sample analysis from screening through counting took about three days.

In attrition runs the entire bed material, including the fines on the filters and on the walls was collected and screened. Samples were taken at the top and bottom position of the bed and screened separately to check for any segregation effect in the bed. The following screens were employed for attrition run samples: -20+30, -30+40, -40+50, -50+70, -70+100, -100+140, -140+200, and a bottom pan for the -200 fraction. Screening time on the Ro-Tap machine was ten minutes.

IV. DATA ANALYSIS

The fundamental dependent variable which indicates changes in particle size is the average diameter of the particles. However, there are numerous ways to define the average diameter⁽¹⁰⁾ depending on what property or properties of the particle are to be accentuated. The average diameter most appropriate and most commonly employed in work related to spray drying is the volume-surface mean diameter, also referred to as the Sauter mean diameter, defined as:

$$D_{vs} = \frac{\sum_i N_i D_i^3}{\sum_i N_i D_i^2} \quad (28)$$

where N_i is the number of particles on the i^{th} sieve and D_i the average size of the particles on that sieve, taken as the arithmetic average of the openings of the two successive screens that bracket this particular sieve fraction. The summation is taken over the number of sieves used in the screen analysis.

The choice of this definition for average diameter is logical when it is recalled that the basic hypothesis for changes in particle size is expressed as the proportionality between the rate of change of the mass of a particle and its surface area. As mass is directly proportional to volume, it is then clear that an average diameter relating volume and surface area is necessary to describe the growth phenomenon.

Equation (28) can be simplified for calculations. Since

$$N_i = \frac{w_i}{\rho_s^b D_i^3} \quad (29)$$

where b the volume shape factor, and ρ_s the solid density are constant for a given material, then substituting equation (29) into equation (28), factoring out the constants and cancelling, there is obtained the working equation for calculations:

$$D_{vs} = \frac{\sum w_i}{\sum \frac{w_i}{D_i}} = \frac{\bar{W}}{\sum \frac{w_i}{D_i}} \quad (30)$$

where $\bar{W}$ is the weight of the entire sample.

Growth Runs:

For growth runs, the change in D_{vs} with time of the seed-containing particles is followed. The D_{vs} is calculated from the screen analysis data and the gamma count data in the following sequence.

Recall the definition of D_{vs} :

$$D_{vs} = \frac{\sum N_i D_i^3}{\sum N_i D_i^2} \quad (28)$$

Here N_i is the number of particles that contain seeds in the i^{th} sieve fraction. The seeds are of size D_0 with activity A_0 counts/minute/gram. From the screen analysis and the gamma count the weight w_i and the activity A_i in counts/minute/gram of the i^{th} fraction are known. $A_i w_i$ then represents the total activity in counts/minute of the i^{th} fraction. This product divided by A_0 yields the weight of seeds in the i^{th} fraction. This last number divided by the weight per seed particle, $\rho_s b D_0^3$, yields the number of seed particles in the i^{th} fraction. Assuming on the whole each seed-containing particle in the i^{th} fraction contains only one seed, then the number of seed particles equals the number of particles containing seeds,

N_i . Thus, summarizing:

$$N_i = \frac{A_i w_i}{A_o \rho_s b D_o^3} \quad (31)$$

Since the group $A_o \rho_s b D_o^3$ is constant for each fraction, it is factored out from the summation sign and cancelled between numerator and denominator in equation (28). This results in the working equation:

$$D_{vs} = \frac{\sum A_i w_i D_i^3}{\sum A_i w_i D_i^2} \quad (32)$$

A typical calculation is shown in Table 1.

Figure 4 gives a plot of the screen analysis data versus time for Run PS-19. Figure 5 shows a plot of activity versus time for the various fractions in Run PS-19. The movement of activity peaks through successive screen fractions clearly indicates the path of growth. It is seen that as time progresses, the activity peaks become lower as the total activity in the bed decreases with the removal of seeds in the product. Thus, a moderate "background" activity due to contact contamination would obscure the activity peaks of the larger-size fractions. For this reason, in some runs where this situation existed, data for calculating D_{vs} were taken from the earlier part of the run where the activity peaks were high and background effect was not pronounced. A summary of D_{vs} as a function of time for all the runs is found in the Appendix.

Having obtained the values of D_{vs} for each sample in a run, the next step is to correlate them with time. From an earlier section, an equation for particle growth was derived relating D_{vs} with time, namely,

$$D_{vs} = D_o + a\theta_F \quad (25)$$

Table 1. Typical Calculation of Average Diameter, D_{vs}

(Run PS-19, Sample 11, taken at 5.5 Hours)

Screen Mesh	A_i c/m/g	w_i gm	D_i x 10^2 in.	D_i^2 x 10^4 in. ²	D_i^3 x 10^6 in. ³	$A_i w_i D_i^2$ x 10^4 in. ²	$A_i w_i D_i^3$ x 10^6 in. ³	D_{vs} x 10^2 in.
-20 +30	12	8.4	2.82	7.95	22.4	0.08×10^4	0.23×10^4	
-30 +40	15	15.7	1.99	3.96	7.88	.09	.19	
-40 +50	75	13.0	1.41	1.99	2.80	.19	.27	
-50 +70	9.1×10^3	6.2	1.00	1.00	1.00	5.64	5.64	
-70 +100	1.16×10^3	0.8	0.71	0.504	0.358	<u>.05</u>	<u>.03</u>	
						6.05	6.36	1.052

Figure 4. Screen Analysis Data as Function of Time for Run PS-19

Figure 5. Particle Activity as Function of Time for Run PS-19

If this equation describes the growth situation satisfactorily, then D_{vs} should vary linearly with time at the rate of the overall growth constant, λ . To test this hypothesis, the best statistical straight line, the least-square line, is calculated for the set of data points^(46,62). From statistical theory the least-square line is the best correlation between two variables when the uncertainty in one variable is insignificant compared to that of the other and the uncertainty in the other is random. This situation prevails here as time can be accurately determined while that involved in determining D_{vs} accrues from the uncertainty in gamma counting. But the disintegration process is random, and hence the uncertainty associated with D_{vs} is random and not systematic.

Using standard methods for calculating the constants for the least-square line,

$$D_{vs} = \lambda' + \gamma (\theta_F - \bar{\theta}_F) \quad (33)$$

where $\bar{\theta}_F$ is the arithmetic mean of all the time values, the constants are given by the following expressions:

$$\lambda' = \bar{D}_{vs} \quad (34)$$

$$\gamma = \frac{\sum \theta_{Fi} D_{vs_i} - \frac{1}{n} (\sum \theta_{Fi} \sum D_{vs_i})}{\sum \theta_{Fi}^2 - \frac{1}{n} (\sum \theta_{Fi})^2} \quad (35)$$

where n is the number of observations. Then combining λ' and $\gamma \bar{\theta}_F$, there results the following equation:

$$D_{vs} = \lambda + \gamma \theta_F \quad (36)$$

where $\lambda = \lambda' - \gamma \bar{\theta}_F$. These calculations are summarized for each run in the Appendix.

After obtaining these constants, it is necessary to determine how well the straight line correlates the data. This test of correlation is essential because although it has been shown that the least-square approximation is the best, it remains to be shown whether a straight line is the best correlating function. To this end, after obtaining the least-square constants λ and γ , values of the average diameter are predicted from the straight line equation at various time, θ_F . Let this predicted value be D_{vs}^* . Then two sums are calculated, $\sum (D_{vs_i}^* - D_{vs_i})^2$ and $\sum (D_{vs_i} - \bar{D}_{vs})^2$. It can be shown⁽⁶²⁾ that by substituting $D_{vs}^* = \lambda + \gamma \theta_F$

$$\sum (D_{vs_i}^* - D_{vs_i})^2 = \sum (D_{vs_i} - \bar{D}_{vs})^2 - \gamma^2 \sum \theta_{Fi}^2 D_{vs_i} \quad (37)$$

where $\sum \theta_{Fi} D_{vs_i} = \sum \theta_{Fi} D_{vs_i} - \frac{1}{n} (\sum \theta_{Fi} \sum D_{vs_i})$. From (37) it is seen

that the term $\gamma^2 \sum \theta_{Fi}^2 D_{vs_i}$ represents the portion of the sum of squares of deviation of the original data removed by the linear correlation. The remainder that is not accounted for and usually attributed to error is the term $\sum (D_{vs_i}^* - D_{vs_i})^2$. The ratio of the sum of squares removed by the correlation to the sum of squares of the original data is a measure of the goodness of the correlation. The square root of this ratio is the correlation coefficient r ,

$$r^2 = \frac{\gamma^2 \sum \theta_{Fi}^2 D_{vs_i}}{\sum (D_{vs_i} - \bar{D}_{vs})^2} = \frac{\sum (D_{vs_i} - \bar{D}_{vs})^2 - \sum (D_{vs_i}^* - D_{vs_i})^2}{\sum (D_{vs_i} - \bar{D}_{vs})^2} \quad (38)$$

For perfect correlation, there is no residual deviation of D_{vs} from D_{vs}^*

and $r^2 = 1.0$. A value of $r^2 = 0.0$ indicates no correlation at all between the two variables D_{vs} and Θ_F . For a given number of degrees of freedom, D. F. = $n-2$, statistical tables are available⁽¹³⁾ that give the probability of a larger value of r . For example, these calculations for Run PS-19 are summarized in Table 2, yielding a value for $r^2 = 0.98$ and $r = 0.99$. From

Table 2. Summary of Data Analysis for Run PS-19
(For Calculation of the Terms see Appendix)

$$D_{vs}^* = 0.00754 + 0.0006885 \Theta_F \qquad \bar{D}_{vs} = 0.01511$$

$$\sum (D_{vs_i}^* - D_{vs_i})^2 = 0.00001645$$

$$\sum (D_{vs_i} - \bar{D}_{vs})^2 = 0.00080122$$

$$r^2 = 0.980$$

$$r = 0.99$$

$$n = 43$$

$$s_p^2(D_{vs_i}) = 1.9077 \times 10^{-5}$$

$$s_e^2(D_{vs_i}) = 4.0158 \times 10^{-7}$$

$$s_e(D_{vs_i}) = \pm 0.000635$$

$$F = 47.50$$

$$D_{vs_i} = D_{vs_i} \pm 0.000635$$

$$s_e^2(\gamma) = 2.4257 \times 10^{-10}$$

$$s_e(\gamma) = \pm 1.56 \times 10^{-5}$$

$$\gamma = 0.0006885 \pm 0.0000156$$

the statistical table for D. F. = $43-2 = 41$, r at the 0.05 probability level is 0.304, i. e., there is only a 0.05 chance of obtaining an r value of 0.304 or larger with 41 degrees of freedom when there is no correlation

between the variables. As a matter of fact, r at the 0.001 probability level for D. F. = 41 is only 0.490. Thus, it is clearly shown that the use of linear correlation is a very good one.

Another test for significance of correlation is the F-test⁽⁴⁶⁾.

The best measure of the precision with which the points fit the correlation line is the "variance of estimate",

$$s_e^2(D_{vs_i}) = \frac{\sum (D_{vs_i}^* - D_{vs_i})^2}{n-2} \quad (39)$$

An estimate of the population variance is

$$s_p^2(D_{vs_i}) = \frac{\sum (D_{vs_i} - \bar{D}_{vs})^2}{n-1} \quad (40)$$

An estimate of the validity of the linear behavior of the data may be obtained by calculating a statistic F :

$$F = \frac{s_p^2(D_{vs_i})}{s_e^2(D_{vs_i})} \quad (41)$$

Standard statistical tables are available that list, for a given D. F., the probability levels for finding values of F greater than the calculated ones. For example, referring to Table 2, in PS-19, $F = 47.5$. From the F -tables, with D. F. = 42 for s_p^2 and 41 for s_e^2 at the 0.01 probability level, the listed value of F is about 2. This means that at the given D. F. there is only a 0.01 chance of erroneously accepting as significant a correlation that gives an F value of 2. Thus, with $F = 47.5$ the correlation is very significant indeed.

When the F -test proves the correlation significant, $s_e^2(D_{vs_i})$ may be used as the best estimate of the precision of the data. So, for ¹ PS-19,

$s_e^2(D_{vs_i}) = 40.16 \times 10^{-8}$ and hence the precision of D_{vs} is ± 0.000635 inches for values of D_{vs} ranging from 0.00820 to 0.0227 inches. More importantly, the best estimate of the precision of the growth constant, γ , is given by

$$s_e^2(\gamma) = \frac{s_e^2(D_{vs_i})}{\sum (\theta_{Fi} - \bar{\theta}_F)^2} \quad (42)$$

For PS-19, the precision of γ is then, from Table 2, $\pm 1.56 \times 10^{-5}$ inches/hr. So γ is between 0.000673 and 0.000704 inches/hr.

A summary of these statistical calculations for each run is included in the Appendix. A summary of the overall growth constants of all of the runs at their respective experimental conditions is presented in Table 3.

In Table 3, the superficial fluidizing velocity was based on column temperature and pressure. The atomizing air rate was calculated at column pressure but at room temperature. Because the atomizing air was not pre-heated and had only a very short time to be heated in passing through the nozzle, it would be very close to room temperature.

Attrition Runs:

A series of four 24-hour runs was made to check the effect of operating variables on attrition and the relative magnitude of attrition with respect to normal growth. Water was fed in to simulate growth run conditions. The same starting bed composition as that employed in growth runs was used in each attrition run. The operating conditions for these runs are summarized in Table 4.

Table 3. Summary of Calculated Overall Growth Constants and Experimental Conditions.

Run No.	Bed Weight gm	Bed Temp. C	Fluid.*		Feed Conc. wt. %	Feed Rate ml/min	Solids*** Rate gm/hr	Atom. Air Rate		Overall Growth Constant, a 10 ⁴ in/hr
			Air Vel. ft/sec	Atom.** Air Vel. CFM				Feed Rate	Rate	
PS-14	900	400	1.00	0.635	50	15.9	600	1130		6.890
PS-19	900	300	1.05	0.647	50	15.9	600	1150		6.885
PS-20	900	400	0.92	0.588	50	15.9	600	1048		7.055
PS-26	900	300	1.00	0.554	50	15.9	600	986		7.248
PS-45	900	400	1.88	0.526	50	15.9	600	937		6.725
PS-46	900	300	1.26	0.339	50	21.2	800	453		14.24
PS-49	1050	300	1.26	0.336	50	10.2	385	932		3.382
PS-50	1050	300	1.40	0.321	50	10.2	385	890		3.000
PS-52	1000	300	1.28	0.336	33	16.0	368	595		3.782
PS-53	1000	400	1.38	0.339	33	16.1	370	596		3.703
PS-57	1100	400	1.86	0.321	50	10.2	385	890		2.760
PS-58	1100	400	1.88	0.749	50	10.0	378	2120		1.850
PS-59	1100	400	1.86	0.653	50	9.6	364	1930		1.727
PS-60 ⁺	1100	400	1.57	0.329	50	9.6	364	970		2.795
PS-61 [†]	1100	400	1.52	0.329	50	9.6	364	970		2.758

* Fluidizing Air Velocity at column temperature and pressure.

** Atomizing Air Rate at column pressure but room temperature.

*** Solids rate as grams per hour of aluminum nitrate nonahydrate.

+ Surface Tension of feed reduced by 1.63 by adding 0.012 wt. % of "Tween 20"

++ Viscosity of feed increased by 5.15 by adding 0.125 wt. % of "Natrosol"

Table 4. Summary of Operating Conditions for Attrition Runs

Run No.	Column Temp. C	Fluidizing Velocity ft/sec	Water Feed Rate ml/min	Atom. Air Rate
				Feed Rate (volume ratio)
AT- 1	300	1.3	16	660
AT- 1'	400	1.3	16	660
AT- 2	300	1.3	10.4	1370
AT- 4	300	1.8	10.4	1370

For the calculation of D_{vs} , equation (30)

$$D_{vs} = \frac{\bar{W}}{\sum \frac{W_i}{D_i}} \quad (30)$$

is applied directly to the data. A typical example is shown in Table 5.

Effect of sampling location was tested by taking samples from both the top and the bottom of the bed for some runs. A summary of the results of these attrition runs is given in Table 6.

Next, statistical tests are applied to these results to test for significance of the following factors: column temperature, fluidizing velocity, sampling location, and atomizing air to feed ratio. The "Student-t" test is employed, shown in the sample calculation below, for testing the significance of column temperature:

$$d_{\text{VS}, \text{AT-1}} \quad d_{\text{VS}, \text{AT-1}'} \quad x_i = (d_{\text{VS}, \text{AT-1}} - d_{\text{VS}, \text{AT-1}'}) \times 10^3$$

0.3284	0.3329	-4.5
.2904	.2930	-2.6
.2733	.2662	+7.1
.2683	.2416	+26.7

$$\sum x_i = 26.7$$

$$\bar{x} = \sum x_i / n = 26.7 / 4 = 6.68$$

$$\sum x_i^2 = 790.31$$

$$\bar{x} \sum x_i = 178.36$$

$$\sum (x_i - \bar{x})^2 = \sum x_i^2 - \bar{x} \sum x_i = 611.95$$

$$\sigma^2(\bar{x}) = \text{variance of mean} = \frac{\sum (x_i - \bar{x})^2}{n(n-1)} = 50.996$$

$$\sigma = 7.141$$

$$t = \frac{\bar{x}}{\sigma} = \frac{6.68}{7.141} = 0.935$$

From two-sided t-distribution tables for 3 degrees of freedom and 95% confidence, the tabulated value of t is 3.182 for significance. Since the value of t calculated from the data is less than the tabulated one, the observed difference in d_{VS} is random and non-significant. So temperature effect on attrition is non-significant.

A summary of applying the t-test to these runs and the conclusions drawn is presented in Table 7.

Table 5. Calculation of Volume-Surface Mean Diameter
Run AT-1, Sample No. 1 after 6 Hours

<u>Screen Mesh</u>	<u>w_i gm</u>	<u>D_i inch</u>	<u>w_i/D_i</u>
-20 +30	109.9	0.0282	3900.
-30 +40	444.0	.0199	22300.
-40 +50	350.0	.0141	24800.
-50 +70	112.9	.0100	11290.
-70 +100	34.9	.0071	4920.
-100 +140	11.6	.0050	2320.
-140 +200	8.7	.0035	2420.
-200	<u>17.5</u>	.0014	<u>12500.</u>

$$W = 1089.5$$

$$\sum \frac{w_i}{D_i} = 84450.$$

$$D_{vs} = \frac{1089.5}{84450} = 0.0129 \text{ inch}$$

Table 6. Summary of Results of Attrition Runs*

<u>Run No.</u>	<u>d_{vs} in mm. after</u>				
	<u>0-hrs</u>	<u>6-hrs</u>	<u>12-hrs</u>	<u>18-hrs</u>	<u>24-hrs</u>
AT-1	0.4008	0.3284	0.2904	0.2733	0.2683
AT-1'		.3329	.2930	.2662	.2416
AT-2		.2557	.2485	.2489	.2096
			.3279 (bot.)		
			.2776 (top)		
AT-4		.2553	.2526	.2501	.2268
		.3243 (bot.)	.3286 (bot.)		
		.3182 (top)	.2620 (top)		

*d_{vs} calculated by screening entire bed including fine on filters and walls unless otherwise noted in parentheses.

Table 7. Summary of Statistical Tests for 95% Confidence using
"Student-t"

<u>Object of Test</u>	<u>Runs Involved</u>	<u>t_{calcd.}</u>	<u>t_{tabulated}</u>	<u>Conclusion</u>
Temperature Effect on Attrition	AT-1, AT-1'	0.9281	3.182	Non-significant
Fluidizing Air Rate Effect	AT-2, AT-4	1.377	3.182	Non-significant
Sampling Loca- tion Effect	AT-2, AT-4	2.272	4.303	Non-significant
Atomizing Air to Feed Ratio Effect	AT-1, AT-1' AT-2, AT-4	2.066	3.182	Non-significant

After noting the non-significance of temperature, fluidizing air, and sampling location, the data of AT-1 and AT-1' were averaged to give a set of values at an atomizing air to feed ratio of 660, and similarly for AT-2 and AT-4. Then these two sets were used to determine the significance of atomizing air to feed ratio shown in the last line of the above table.

V. CORRELATION OF DATA

Since attrition effect is found to be non-significant then the overall growth constant, a , defined as $\frac{K-C}{3b\rho_s}$ by equation (25) is determined solely by the normal growth coefficient K , i.e.,

$$K = 3b \rho_s^a \quad (43)$$

But K is in turn expressed as

$$K = \frac{kk_1k_2V'_s\rho_s(1-\epsilon)}{W} \left[1 - \frac{\rho_s(1-\epsilon)}{\rho_{bs}} \right] \quad (8)$$

As V'_s , ρ_s , ϵ , ρ_{bs} , and W are known quantities or quantities that can be calculated from the operating data, then the group kk_1k_2 instead of K is correlated with the operating variables. For this purpose, combining equations (8) and (43), a working equation for correlation of kk_1k_2 is derived:

$$K \equiv kk_1k_2 = \frac{3baW}{V'_s(1-\epsilon)} \left[1 - \frac{\rho_s(1-\epsilon)}{\rho_{bs}} \right]^{-1} \quad (44)$$

In the above equation, W is known for each run. V'_s is calculated from the geometry of the column and the characteristics of the spray nozzle through the following equation (see Appendix for derivation):

$$V'_s = \frac{2\pi R^3}{3} \tan^2 \alpha \cos \alpha (2 + \sin^2 \alpha) \quad (45)$$

Substituting the value of 0.125 ft. for R , the radius of the column, and $\alpha = 9^\circ$ for the half spray-angle for the nozzle (Spraying Systems Co.

data), V_s is equal to $2.054 \times 10^{-4} \text{ ft}^3$. The solids density ρ_s and the bulk density ρ_{bs} are determined by direct measurement. The volume shape factor b is calculated. The bed voidage fraction ϵ is calculated from equation (17) or (20) depending on whether the fluidized bed is in the turbulent or laminar region:

$$G = \left(\frac{g_c \rho_F \phi_s}{35.4 \mu_F^{0.44}} \right)^{0.641} \rho_s^{0.641} D_p^{0.923} \frac{\epsilon^{1.923}}{(1-\epsilon)^{0.282}} \quad (17)$$

$$G = \left(\frac{g_c \rho_F \phi_s^2}{116 \mu_F^{0.78}} \right)^{0.82} \rho_s^{0.82} D_p^{1.46} \frac{\epsilon^{2.46}}{(1-\epsilon)^{1.46}} \quad (20)$$

In these equations, G , ρ_F , μ_F are known, while D_p and ϕ_s , the surface shape factor, are separately determined. The first step for correlation, then, is the determination of the particle properties, followed by calculation of ϵ .

Determination of Particle Properties

From Run PS-19 (300°C) density determination by the displacement of xylene method was made for products at the beginning, middle, and end of the run with the following results:

Density in grams per cc

<u>Beginning</u>	<u>Middle</u>	<u>End</u>
2.07	1.61	1.67
2.02	1.72	1.74
1.76	1.74	1.79
1.74		1.62

It is seen that the density variation during the run is not pronounced so an average of all the values is taken as 1.77 gm/cc. Essentially the

same result is obtained from PS-14 (400°C), and so the value of 1.77 gm/cc is used in the calculation of the volume shape factor b.

The volume shape factor b is defined as the factor relating the mass of a particle to its volume through the following relationship:

$$m = \rho_s b D^3$$

To determine b, a weighed sample, M, of a given sieve fraction was taken and the number of particles, N, in this sample was counted. Then using the arithmetic average of the openings of the two successive screens that defined this particular sieve fraction as the diameter of the particles, D,

$$b = \frac{M}{\rho_s N D^3}$$

Four such determinations were made and results summarized for Run PS-19:

<u>Sampling Time, hr</u>	<u>Mesh Size</u>	<u>M gram</u>	<u>N</u>	<u>b</u>
0.5	-40 +50	0.0343	772	0.526
0.5	-20 +30	0.1064	329	0.500
21.5	-20 +30	0.0975	304	0.495
21.5	-30 +40	0.0573	388	0.648

An average is taken of the four values and $b = 0.542$ is used in subsequent work. For a spherical particle, $b = \frac{\pi}{6} = 0.524$. It is thus seen that the particles were quite spherical in shape, confirming a similar conclusion from visual observations. The approach to sphericity is $0.524/0.542 = 0.966$.

The surface shape factor, ϕ_s , for a particle is defined as the ratio of the surface area of a spherical particle having the same volume as the given particle to the surface of that particle. For a sphere, ϕ_s equals unity. For any other shape, ϕ_s is less than unity because a sphere has the minimum surface area for a given volume. The surface area of a particle is not easily determined with accuracy. Since the particles involved in this investigation are nearly spherical, as shown from the volume shape factor calculations, a value of 0.96 is assigned to ϕ_s .

The bulk density, ρ_{bs} , is calculated directly from the weight of a given volume of particles. For each run, bulk density of samples at the beginning and the end of a run was determined and an average taken. Results are summarized in Table 8.

The average size of the particles in the bed at any time, D_p , is taken as the average of the values at the beginning and the end of a run. It is calculated from

$$D_p = \frac{\bar{W}}{\sum \frac{w_i}{D_i}}$$

The results for the runs are summarized in Table 9.

Determination of Bed Voidage Fraction

Either equation (17) or (20) may be used for calculating the bed voidage ϵ . In the laminar region, defined by Chu, et al. as the region where the modified Reynolds Number,

$$Re' = \frac{D_p G}{\mu_F(1-\epsilon)}$$

is less than 30. Above 30 the region is turbulent. Equation (20) is used

Table 8. Bulk Density Determinations

<u>Run No.</u>	<u>Sample Time, hr</u>	ρ_{bs} <u>gm/cc</u>	<u>Average</u>
PS-14	0	0.940	0.951
	12	0.963	
PS-19	0	0.943	0.960
	20	0.978	
PS-20	0.5	0.930	0.950
	14.5	0.970	
PS-26	0.5	0.944	0.916
	28	0.888	
PS-45	1	0.945	0.854
	24	0.762	
PS-46	0	0.935	0.938
	2	0.940	
PS-49	0.5	0.918	0.899
	24	0.880	
PS-50	0.5	0.895	0.829
	24	0.763	
PS-52	0.5	0.920	0.972
	15	1.025	
PS-53	0.5	0.913	0.909
	24	0.905	
PS-57	0.5	0.907	0.898
	24	0.888	
PS-58	0.5	0.944	0.910
	24	0.876	
PS-59	1	1.000	0.943
	24	0.886	
PS-60	1	0.965	0.886
	24	0.806	
PS-61	1	0.972	0.894
	24	0.815	

Table 9. Average Particle Size in the Bed

<u>Run No.</u>	<u>Initial D_p</u> <u>10³ ft.</u>	<u>Final D_p</u> <u>10³ ft.</u>	<u>Avg D_p</u> <u>10³ ft.</u>
PS-14	1.38	1.80	1.59
PS-19	1.31	2.10	1.70
PS-20	1.31	1.92	1.62
PS-26	1.31	1.29	1.30
PS-45	1.31	1.24	1.28
PS-46	1.31	1.35	1.33
PS-49	1.31	1.92	1.62
PS-50	1.31	1.95	1.63
PS-52	1.31	1.60	1.46
PS-53	1.31	1.88	1.60
PS-57	1.31	2.01	1.66
PS-58	1.31	0.585	0.95
PS-59	1.31	0.680	0.94
PS-60	1.31	2.03	1.67
PS-61	1.31	1.80	1.56

and after obtaining the value for ϵ , the Re is calculated to see if it is below 30.

Substituting in equation (20) $G = 3600 V \rho_F$ and $g_c = 4.17 \times 10^8$ ft. lb mass/(lb. force)(hr)² and simplifying:

$$V = \left(\frac{66 \phi_s^{1.64} \rho_s^{0.82} D_p^{1.46}}{\rho_F^{0.18} \mu_F^{0.64}} \right) \frac{\epsilon^{2.46}}{(1-\epsilon)^{1.46}} = \Phi \left[\frac{\epsilon^{2.46}}{(1-\epsilon)^{1.46}} \right] \quad (46)$$

A plot of the group $\epsilon^{2.46}/(1-\epsilon)^{1.46}$ versus ϵ is made in Figure 6.

For each run, the group Φ is determined, then V/Φ , and finally ϵ .

The modified Reynolds Number is then calculated to see if the use of the laminar region equation is correct. To test whether the change in D_p during a run affects the flow characteristics of the fluidized bed, void fraction and Reynolds Number are calculated using values of D_p from the beginning and the end of a run. Run PS-19 showed the greatest change in D_p and was chosen for the test with the following result:

$\frac{D_p}{10^3 \text{ft.}}$	Designation	ϵ	Re
1.31	initial	0.425	6.5
2.10	final	0.530	12.7
1.70	average	0.491	9.5

It is seen that the flow is in the laminar zone and that the variation in ϵ is not great so that an average value may be used. Hence, using average values of D_p , calculations summarized in Table 10 are made.

From the table it is seen that all the Reynolds Numbers calculated are less than 30 and hence the fluidized bed was in the laminar region, as originally assumed.

Figure 6. Relationship between Bed Voidage Fraction ϵ and the Group $\epsilon^{2.46} / (1 - \epsilon)^{1.46}$

Table 10. Summary of Calculation for Bed Voidage Fraction ϵ

Run No.	Column Temp. °C	Column Pressure psig	V Fluid. Air Vel. ft/sec	Φ	V/Φ	ϵ	$(1 - \epsilon)$	$\frac{D_p G}{\mu_F (1 - \epsilon)}$
PS-14	400	2.2	1.00	2.20	0.454	0.488	0.512	5.5
PS-19	300	3	1.16	2.49	0.465	0.491	0.509	9.5
PS-20	400	4.3	0.92	2.21	0.416	0.477	0.523	5.7
PS-26	300	6	1.00	1.64	0.610	0.526	0.474	6.4
PS-45	400	3	1.88	1.59	1.18	0.611	0.389	11.5
PS-46	300	3.5	1.26	1.74	0.725	0.548	0.452	7.7
PS-49	300	3.7	1.26	2.30	0.547	0.512	0.488	10.6
PS-50	400	3.5	1.40	2.25	0.621	0.528	0.472	9.2
PS-52	300	3.7	1.28	1.98	0.645	0.533	0.467	10.1
PS-53	400	3.5	1.38	2.20	0.630	0.530	0.470	9.0
PS-57	400	3.3	1.86	2.33	0.800	0.560	0.440	13.3
PS-58	400	3.0	1.88	1.02	1.84	0.666	0.334	10.0
PS-59	400	3.3	1.86	1.01	1.84	0.666	0.334	9.9
PS-60	400	2.6	1.57	2.36	0.666	0.537	0.463	10.3
PS-61	400	2.7	1.52	2.13	0.715	0.546	0.454	9.6

Correlation of K' with Variables

Having obtained the necessary values in equation (44) the next step is to correlate $K' \equiv k k_1 k_2$ with the variables studied. Let the group of terms

$$\frac{3bW}{v'_s (1-\epsilon)} \left[1 - \frac{\rho_s (1-\epsilon)}{\rho_{bs}} \right]^{-1} \equiv \Psi$$

For each run Ψ is calculated, whence K' . However, the group $\frac{\rho_s (1-\epsilon)}{\rho_{bs}}$ is quite close to unity in a number of runs so that upon taking difference between it and unity any small uncertainty in $\frac{\rho_s (1-\epsilon)}{\rho_{bs}}$ is magnified greatly in the difference. Consequently, as the values of ρ_{bs} for these runs are quite constant and those for ϵ reasonably so, average value of each is used for all the runs. Then

$$\Psi = 1.40 \times 10^5 W$$

The following Table 11 lists the values of K' thus calculated.

Table 11. Calculated Values of K'

Run No.	$\frac{a}{x 10^4} \text{ in/hr.}$	$\frac{W}{\text{lb.}}$	$\frac{K'}{\text{in lb}} \frac{\text{hr ft}^3}{\text{hr ft}^3}$
PS-14	6.890	1.987	191.7
PS-19	6.885	1.987	191.5
PS-20	7.055	1.987	196.2
PS-26	7.248	1.987	202
PS-45	6.725	1.987	187.1
PS-46	14.24	1.987	396
PS-49	3.382	2.32	110.0
PS-50	3.000	2.32	97.5
PS-52	3.782	2.206	116.9
PS-53	3.700	2.206	114.3
PS-57	2.760	2.43	94.0
PS-58	1.850	2.43	63.0
PS-59	1.727	2.43	58.8
PS-60	2.795	2.43	95.2
PS-61	2.758	2.43	94.0

The proposed correlation for K' is:

$$K' = \phi' \left(\frac{F}{W}\right)^{\alpha} B^{\beta} V^{\gamma} T^{\delta} \mu^{\omega} (c\sigma)^{\tau}$$

where F = solids feed rate in gm of hydrated nitrate per hour

B = atomizing air rate/feed rate

V = fluidizing velocity in ft/sec

T = temperature $^{\circ}\text{C}$

W = bed weight in grams

$\alpha, \beta, \gamma, \delta, \omega, \tau$ are constants

μ = viscosity of feed in lb/(ft. hr)

σ = surface tension of feed in dynes/cm

$c\sigma$ = surface tension in lb/ft, where c is a conversion factor.

Combining the constants c and ϕ' , the above equation becomes:

$$K' = \phi \left(\frac{F}{W}\right)^{\alpha} B^{\beta} V^{\gamma} T^{\delta} \mu^{\omega} \sigma^{\tau} \quad (47)$$

The variables included in the above equation are the ones studied. The use of F/W instead of F is apparent because it is the amount of feed available to each particle that contributes to growth. Thus for the same solids feed rate the larger the total bed weight the less the growth as there are more particles over which to distribute the feed. The form is reasonable because the variables chosen have, from physical considerations, only primary action on the value of K' and no interactions between them. This means, for example, that V and B individually act on K' , but V and B do not act on each other such that their combined action affects K' . Put in another way, V and B each affect K' but they do not affect each other. This is the interpretation of first order interactions of the independent variables on the dependent variable. This interpretation can be extended to

higher order interactions and they are found to be absent also. It is known that the combined effect of a group of variables not mutually dependent is best described by a product form. This type of expression is common, for example, in heat and mass transfer coefficient correlation where the combined effect of a number of dimensionless groups that do not interact with each other is expressed as a product of some power of each dimensionless group. To evaluate the various exponents in (47) it is clear that by taking ratio of K' for two runs the constant term ϕ is cancelled between them. Thus

$$\frac{K_1'}{K_2'} = \left(\frac{F_1 W_2}{F_2 W_1} \right)^\alpha \left(\frac{B_1}{B_2} \right)^\beta \left(\frac{V_1}{V_2} \right)^\gamma \left(\frac{T_1}{T_2} \right)^\delta \left(\frac{\mu_1}{\mu_2} \right)^\omega \left(\frac{\sigma_1}{\sigma_2} \right)^\tau \quad (48)$$

Furthermore, by taking a pair of runs in which all the variables except one, say B, is held constant, then only one ratio on the right hand side of equation (48) is different from unity, i. e., $\frac{B_1}{B_2}$. By forming similar ratios between pairs of runs and then plotting on log-log paper

$$\frac{K_1'}{K_2'} \text{ vs. } \frac{B_1}{B_2}, \text{ if a straight line through the point (1,1) should result,}$$

then the slope of this line is the desired exponent β . In analagous manner the exponents of the other variables are determined. Finally, ϕ is calculated by inserting in equation (47) the values for K' , F/W , B , V , T , μ , and σ . The goodness of the fit of equation (47) to the data is measured first by the degree of linearity in plotting the above-mentioned ratios, and secondly by the constancy of ϕ calculated from all the runs.

The nitrate concentration, upon which μ and σ depend, only assumed two values. For most of the runs, 50% concentration was used. Hence in taking ratios, these two terms cancel. They are temporarily omitted from

consideration and their effects are evaluated after the operating variables have been correlated. Referring to the summary of results in Table 3, it is seen that there are a number of pairs of runs in which practically only the atomizing air to feed ratio was changed. Hence this factor is correlated first. For the moment, the small variation in the other factors is neglected. An iterative process follows whereby the exponents determined from the first iteration are used to check the effect of small changes in some variables neglected in the first iteration. If these changes are significant then a second and further iterations are carried out as needed.

From Table 3, the pairs of runs shown in Table 12 are selected for study of the exponent β of the term B in equation (47). The last two columns of the table indicate the ratios formed between the pairs, neglecting the small changes in F/W and V for the time being.

Table 12. Pairs of Runs to Determine β

Run No.	T $^{\circ}\text{C}$	V ft/sec.	F/W hr^{-1}	B	K'	$\frac{Z_1^*}{Z_2}$	$\frac{B_1}{B_2}$
PS-14	400	1.00	0.667	1130	191.7	1.024	0.927
PS-20	400	0.92	0.667	1048	196.2		
PS-19	300	1.05	0.667	1150	191.5	1.055	0.858
PS-26	300	1.00	0.667	986	202		
PS-50	400	1.40	0.367	890	97.5	1.174	0.670
PS-53	400	1.38	0.370	596	114.3		
PS-57	400	1.86	0.350	890	94.0	1.492	0.420
PS-58	400	1.88	0.344	2120	63.0		

$$* \frac{Z_1}{Z_2} = \left(\frac{K_1'}{K_2'} \right) \left(\frac{F_2 W_1}{F_1 W_2} \right)^{\alpha} \left(\frac{V_2}{V_1} \right)^{\gamma} \left(\frac{T_2}{T_1} \right)^{\delta}$$

A plot of $\frac{Z_1}{Z_2}$ versus $\frac{B_1}{B_2}$ on log-log paper is shown in Figure 7, exhibiting a satisfactory linear relationship between the variables. Using least-square

Figure 7. Determination of the Exponent β in the Correlation Equation for K'

method on the data points, the following Table 13 is constructed to summarize the procedure:

Table 13. Calculation of Constants for Linear Least-Square Correlation

$\frac{10B_1}{B_2}$	$x_i = \log \frac{10B_1}{B_2}$	x_i^2	$\frac{10Z_1}{Z_2}$	$y_i = \log \frac{10Z_1}{Z_2}$	$x_i y_i$
9.27	0.96708	0.93524	10.24	1.01030	0.97704
8.58	.93349	.87140	10.55	1.02325	.95519
6.70	.82607	.68239	11.74	1.06967	.88362
4.20	.62325	.38844	14.92	1.17377	.73155
*10.00	1.00000	1.00000	10.00	1.00000	1.00000

*The point (1,1) is always on such a ratio-type correlation

$$\sum x_i = 4.34989$$

$$\sum y_i = 5.27699$$

$$\bar{x} = \frac{\sum x_i}{5} = 0.86998$$

$$\bar{y} = \frac{\sum y_i}{5} = 1.05540$$

$$\sum x_i^2 = 3.87747$$

$$\sum x_i y_i = 4.54740$$

$$\bar{x} \sum x_i = 3.78432$$

$$\bar{x} \sum y_i = 4.59087$$

$$\beta = \text{slope} = \frac{-0.04347}{0.09315} = -0.467$$

$$\frac{Z_1}{Z_2} = 0.990 \left(\frac{B_1}{B_2} \right)^{-0.467} \quad (49)$$

Next, the exponent γ of V is determined using exactly analogous procedures except that now the runs with different values for B may be included since β is known. The following Table 14 lists the runs chosen:

Table 14. Pairs of Runs to Determine γ

Run No.	T	V	F/W	B	K'	$\frac{Z_1^*}{Z_2}$	$\frac{V_1}{V_2}$
PS-20	400	0.92	0.667	1048	196.2		
PS-45	400	1.88	0.667	937	187.1	1.148	0.489
PS-50	400	1.40	0.367	890	97.5		
PS-57	400	1.86	0.350	890	94.2	1.037	0.752
PS-53	400	1.38	0.370	596	114.3		
PS-58	400	1.88	0.344	2120	63.0	0.99	1.36

$$* \frac{Z_1}{Z_2} = \frac{K_1'}{K_2'} \left(\frac{F_2 W_1}{F_1 W_2} \right)^\alpha \left(\frac{B_2}{B_1} \right)^{-0.467} \left(\frac{T_2}{T_1} \right)^\delta$$

Plot of $\frac{Z_1}{Z_2}$ versus $\frac{V_1}{V_2}$ is made on Figure 8. Following similar least-square calculations as before:

$$\gamma = -0.147$$

and

$$\frac{Z_1}{Z_2} = 1.014 \left(\frac{V_1}{V_2} \right)^{-0.147} \quad (50)$$

Now having β and γ , the next exponent to be determined is δ . For this, the following runs are selected in Table 15. As seen from the last two columns of the table below, the points cluster around unity for different values of the temperature ratio. Hence, temperature is considered not to have any effect on particle growth, and δ is taken as zero, eliminating T as a variable. This agrees with observations and also with the calculated overall growth constant, a , in the summary. Note the closeness of the values of a for PS-14, PS-19, and PS-52, PS-53 where the only variable changed was temperature.

Figure 8. Determination of the Exponent γ in the Correlation Equation for K'

Table 15. Pairs of Runs to Determine δ

Run No.	T	V	F/W	B	K'	$\frac{Z_1^*}{Z_2}$	$\frac{T_1}{T_2}$
PS-14	400	1.00	0.667	1130	191.7	0.994	1.333
PS-19	300	1.05	0.667	1150	191.5		
PS-20	400	0.92	0.667	1048	196.2	0.986	1.333
PS-26	300	1.00	0.667	986	202		
PS-49	300	1.26	0.367	932	110.0	1.122	0.75
PS-50	400	1.40	0.367	890	97.5		
PS-52	300	1.28	0.368	595	116.9	1.01	0.75
PS-53	400	1.38	0.370	596	114.3		

$$\frac{Z_1}{Z_2} = \left(\frac{K_1'}{K_2} \right) \left(\frac{F_2 W_1}{F_1 W_2} \right)^\alpha \left(\frac{B_2}{B_1} \right)^{-0.467} \left(\frac{V_2}{V_1} \right)^{-0.147}$$

Finally, the exponent α for F/W is determined. As only three sufficiently different values of F/W were available, ratios of these three runs are formed as shown in Table 16.

Table 16. Pairs of Runs to Determine α

Run No.	V	F/W	B	K'	$\frac{Z_1^*}{Z_2}$	$\frac{F_1 W_2}{F_2 W_1}$
PS-19	1.05	0.667	1150	191.5	2.16	1.84
PS-52	1.28	0.368	595	116.9		
PS-46	1.26	0.890	453	396	1.38	1.333
PS-19	1.05	0.667	1150	191.5		
PS-46	1.26	0.890	453	396	2.98	2.42
PS-52	1.28	0.368	595	116.9		

$$\frac{Z_1}{Z_2} = \left(\frac{K_1'}{K_2} \right) \left(\frac{B_2}{B_1} \right)^{-0.467} \left(\frac{V_2}{V_1} \right)^{-0.147}$$

Figure 9 shows the linear relationship. Making calculations for the least-square constants, the result is that:

$$\frac{Z_1}{Z_2} = 0.9886 \left(\frac{F_1 W_2}{F_2 W_1} \right)^{1.25} \quad (51)$$

As the coefficients in equation (49), (50), and (51) are very nearly unity, the correct value if the proposed correlation described the situation exactly, combining the three equations and taking the average value of these constants as unity, there is obtained:

$$K' = k k_1 k_2 = \phi \left(\frac{F}{W} \right)^{1.25} B^{-0.467} V^{-0.147} \quad (52)$$

Now that the operating variables have been correlated, the physical properties of feed viscosity and surface tension are next considered. The following data of these two variables were taken:

<u>Type of Feed</u>	<u>μ lb/ ft. hr.</u>	<u>σ dynes/cm</u>
33%	4.33	67.3
50%	7.84	65.7
50% with surface additive	8.87	40.3
50% with viscosity additive	45.7	70.0

Since it is observed that viscosity changes somewhat with surface tension and vice versa, they cannot be separately determined. Consequently, two pairs of runs are used to solve for the two exponents ω and τ simultaneously. Taking PS-59, PS-60, and PS-59, PS-61 and using the exponents of the operating variables previously determined, there results:

Figure 9. Determination of the Exponent α in the Correlation Equation for K'

$$0.875 = 0.1717^{\omega} 0.931^{\tau}$$

$$0.871 = 0.883^{\omega} 1.482^{\tau}$$

Solving these two equations,

$$\omega = 0.0628$$

$$\tau = -0.321$$

To check the effect of these variables, ratio of K' are taken for PS-50 and PS-52 having different feed concentrations. First, without including μ and σ the ratio shows, referring to equation (52), a value of 0.834 on the left-hand side and 0.817 on the right-hand side. Then including μ and σ , the right-hand becomes 0.855. Without using them the agreement between the two sides of the equation is 0.98, while using them 0.98. The effect of these two factors are small as expected from observation and the work of Wallman and Blyth⁽⁶³⁾.

Incorporating the viscosity and surface tension into the correlating equation:

$$K' \equiv k k_1 k_2 = \phi \left(\frac{F}{W} \right)^{1.25} B^{-0.467} V^{-0.147} \mu^{0.0628} \sigma^{-0.321} \quad (53)$$

Next, equation (53) is used to check if significant error has been introduced in its derivation by neglecting small changes in some variables. To this end, Table 17 is now constructed from Tables 12, 14, and 16, in which each of these previously neglected variable ratios raised to its proper power is included and these values checked against unity.

Plotting these adjusted $\frac{Z_1}{Z_2}$ values on Figures 7 and 8, it is seen that these points fall very close to the lines obtained in the first iteration. Consequently, no modifications of the exponents are necessary and equation (53) stands as it is.

Table 17. Check on Neglected Variable Ratios in First Iteration

Table No.	Run Pair	$\left(\frac{V_2}{V_1}\right)^{-0.147}$	$\left(\frac{F_2 W_1}{F_1 W_2}\right)^{1.25}$	$\left(\frac{\mu_2}{\mu_1}\right)^{0.0628}$	$\left(\frac{\sigma_2}{\sigma_1}\right)^{-0.321}$	Adjusted $\frac{Z_1}{Z_2}$
12	PS-14 PS-20	0.988				1.012
	PS-19 PS-26	1.00				1.055
	PS-50 PS-53	1.00	0.990	1.046		1.217
	PS-57 PS-58	1.00	0.979			1.462
14	PS-53 PS-58		0.923	1.046		0.962
	PS-50 PS-57		0.956			0.983

The final step is to calculate ϕ from each run through equation (53) and see how constant it is. The results are tabulated in Table 18.

It is seen that ϕ for the different runs does not vary much, the average value being 2.95×10^4 .

Thus, the final form of the correlation equation

$$K' = k k_1 k_2 = 2.95 \times 10^4 \left(\frac{F}{W}\right)^{1.25} B^{-0.467} V^{-0.147} \mu^{0.0628} \sigma^{-0.321} \quad (54)$$

and

$$K = \frac{9.83 \times 10^3 \left(\frac{F}{W}\right)^{1.25} B^{-0.467} V^{-0.147} \mu^{0.0628} \sigma^{-0.321} V_s' (1-\epsilon)}{bW}$$

$$\left[1 - \frac{\rho_s (1-\epsilon)}{\rho_{bs}} \right] \quad (55)$$

Table 18. Determination of ϕ in K' Correlation

Run No.	F/W hr^{-1}	B	V $ft/sec.$	$(F/W)^{1.25}$	$B^{-0.467}$	$V^{-0.147}$	$\mu^{0.0628}$ $\sigma^{-0.321}$	K' $\frac{in\ lb}{hr\ ft^3}$	ϕ $\times 10^{-4}$
PS-14	0.667	1130	1.00	0.602	0.0375	1.00	0.296	191.7	2.86
PS-19	0.667	1150	1.05	0.602	0.0372	0.931	0.296	191.5	3.10
PS-20	0.667	1048	0.92	0.602	0.0389	1.016	0.296	196.2	2.79
PS-26	0.667	986	1.00	0.602	0.0400	1.00	0.296	202	2.84
PS-45	0.667	937	1.88	0.602	0.0410	0.911	0.296	187.1	2.81
PS-46	0.890	453	1.26	0.863	0.0573	0.967	0.296	396	2.80
PS-49	0.367	932	1.26	0.285	0.0410	0.967	0.296	110.0	3.28
PS-50	0.367	890	1.40	0.285	0.0418	0.952	0.296	97.5	2.89
PS-52	0.368	595	1.28	0.286	0.0504	0.964	0.284	116.9	2.96
PS-53	0.370	596	1.38	0.288	0.0504	0.954	0.284	114.3	2.91
PS-57	0.350	890	1.86	0.268	0.0418	0.913	0.296	94.0	3.10
PS-58	0.344	2120	1.88	0.263	0.0280	0.911	0.296	63.0	3.16
PS-59	0.331	1930	1.86	0.250	0.0292	0.913	0.296	58.8	2.97
PS-60	0.331	970	1.57	0.250	0.0415	0.936	0.350	95.2	2.80
PS-61	0.331	970	1.52	0.250	0.0415	0.940	0.326	94.0	2.95

For this investigation, the above equation is also that of the overall growth constant, a , since attrition effect is found to be non-significant, and hence $K = a$.

VI. DISCUSSION OF RESULTS

Results from the Present Investigation

From the data analysis of each run a linear relationship between the change in the average diameter of particles containing seeds and time exhibits very strong correlation, shown by the fact that in every case the correlation coefficient, r , is greater than 0.95. A perfect correlation would have $r = 1.0$. This confirms the original hypothesis that the particle growth rate is proportional to the surface area of a particle. Similar result was reported by Griffin, et al.⁽²⁰⁾ in their fluidized coker. The average estimated precision of the overall growth constants is $\pm 6\%$. It has thus been demonstrated that the use of radioactive tracer is a good method to follow particle growth in a fluidized calciner. The technique developed in this investigation is original.

The reproducibility of the data has been checked through two runs, PS-59 duplicating PS-58, and PS-26 duplicating PS-19. A 6.6% difference between the overall growth constants for PS-58 and PS-59 is accounted for by the slightly lower feed rate in PS-59, and a 5% difference between the overall growth constants for PS-19 and PS-26 is accounted for by the higher value of atomizing air to feed ratio in PS-19. (See Table 3.) Thus, on the whole, it can be said that the reproducibility of data is good.

The range of variations in the factors under study was limited by the equipment and the inherent nature of fluidized calcination process. Extension of the range resulted in instability of operation followed by caking of the bed. The extremes of the variation in operating variables presented in Table 19 represented limiting operating conditions consistent with continuous operation.

Table 19. Range of Variation in the Variables Studied

<u>Variable</u>	<u>Range</u>
Fluidizing Velocity	0.92 - 1.88 ft/sec
Temperature	300 - 400 C
Atomizing air to feed ratio	453 - 2120
Feed Rate to bed weight ratio	0.331 - 0.889
Surface tension of feed	40.3 - 70.0 dynes/cm
Viscosity of feed	4.33 - 45.7 lb/(hr ft)

The correlation of the normal growth coefficient, K, is represented by

$$K = \frac{9.83 \times 10^3 \left(\frac{F}{W}\right)^{1.25} B^{-0.467} V^{-0.147} \mu^{0.0628} \sigma^{-0.321} V_s' (1-\epsilon)}{bW}$$

$$\left[1 - \frac{\rho_{s(1-\epsilon)}}{\rho_{bs}} \right] \quad (55)$$

Since in this investigation, attrition effect is found to be non-significant, the above equation is also that of the overall growth constant, a. This equation correlates the data of this investigation to an average absolute deviation of 4% and arithmetic average of 0.07%. The number of variables included in this equation, characteristic of the feed system and the operating conditions, indicates that the equation may be applied to cover a fairly wide range of systems and operations. The exponents of the various terms in the above equation agree with the expected trend in variation. Increasing the value of F/W causes an increase in the growth rate because more feed solids is then available per particle. The negative exponents of B and V indicate that if these variables are increased

a decrease in growth would follow, due likely to the creation of more fine particles. The smaller exponent of V compared to that of B indicates that the creation of fine particles is controlled by B , as expected. The fluidizing velocity changes the voidage fraction, ϵ , but the group

$(1-\epsilon) \left[1 - \frac{\rho_s(1-\epsilon)}{\rho_{bs}} \right]$ is to a large degree self-compensating. That is to say, if ϵ is decreased, then $(1-\epsilon)$ is increased, causing an increase in $\frac{\rho_s(1-\epsilon)}{\rho_{bs}}$ and a consequent decrease in $1 - \frac{\rho_s(1-\epsilon)}{\rho_{bs}}$. So the product

of $(1-\epsilon)$ and $1 - \frac{\rho_s(1-\epsilon)}{\rho_{bs}}$ may not change, or change little. Thus,

the overall effect of V is probably small. The absence of temperature effect is an indication that the effect of chemical reaction, that is, the calcination of aluminum nitrate to oxide, is negligible. The term V'_s which is characteristic of the size of the fluidized column and the spray nozzle increases with larger columns. However, in a larger column there is also more solids so W is larger. Thus V'_s/W is also somewhat self-compensating. The effect of physical properties of the feed is minor.

For the steady-state operation seeds must be introduced into the calciner to balance the normal growth, which has been shown in this study to far outweigh the attrition effect from the atomizing air. Direct addition of seeds to the calciner is one possibility. Other methods of creating seeds such as jet grinding or target grinding have been reported⁽²⁰⁾. In jet grinding a high velocity jet of air is directed against the particles in the bed, whereas in target grinding the air jet is directed against a metal target mounted in the bed. The relationship between the jet air input, jet velocity and extent of attrition would be determined empirically. Having the attrition data to counteract normal growth, conditions

for no net particle growth can be derived and steady-state operation achieved. Such attrition studies, however, are beyond the scope of this investigation.

Comparison with Results from Other Investigations

Results from some earlier work done at the Argonne National Laboratory by E. J. Petkus⁽³⁰⁾ and the work carried on at present at the Idaho Chemical Processing Plant under E. S. Grimmett⁽²²⁾ are compared with the results obtained in this investigation. Work at Argonne was done in a 6-inch diameter column while at Idaho a 2-ft. square unit was employed. Comparisons with the results from the 3-inch unit used in this work would afford a means of estimating the scale-up factor of the fluidized calciner.

The feed concentration used in the runs at Argonne and Idaho were 2.12 M aluminum nitrate nonahydrate equivalent to 58.8 weight per cent. The operating conditions for these runs are summarized:

<u>Operating Variables</u>	<u>Argonne</u>		<u>Idaho</u>	
	<u>WC-1</u>	<u>WC-2</u>	<u>SA-1</u>	<u>SA-2</u>
Temperature °C	400	400	500	500
Fluidizing velocity ft/sec	1.50	1.54	0.64	0.85
Feed rate, ml/min	103	184	667	667
Solids feed rate gm/hr	4940	8620	31800	31800
<u>Atomizing air rate</u> Feed rate	339	195	382	254
Bed weight, kg	4.0	4.0	153	160.4
F/W	1.235	2.154	0.208	0.198

Since the feed solution was close to the 50 wt% one used in this work, the physical properties were considered the same. Moreover, as no

attrition data were given for these runs, it was assumed that attrition was not significant and that the normal growth was equal to overall growth.

Applying equation (55), the predicted growth constants were obtained. In the Argonne work, overall growth constants were calculated from screen analysis data by using least square method on the D_{vs} , with correlation coefficient for a linear fit greater than 0.98. Similar data were not available from the Idaho work, but values for growth constants were reported. These values of growth constants are presented:

	<u>WC-1</u>	<u>WC-2</u>	<u>SA-1</u>	<u>SA-2</u>
Predicted growth constant, in/hr	0.00457	0.01158	0.00126	0.001308
Actual growth constant, calculated or reported, in/hr	0.001644	0.002334	0.0000945	0.000134

Now taking ratios of the predicted growth constant and the actual value and averaging them for the runs in the 6-inch and 27.1-inch units, the following results are obtained:

<u>Column Diameter, inches</u>	<u>Avg. Ratio of Growth Constants</u>
3	1
6	3.87
27.1	11.54
(equivalent to 2-ft. square)	

Plotting the average ratio versus the reciprocal of the column diameter D_c , a straight line is obtained, shown in Figure 10 with the equation

$$\frac{a_{\text{predicted}}}{a_{\text{actual}}} = 15.6(10)^{-3.61/D_c}$$

Figure 10. Average Ratio of Predicted and Calculated Growth Constants as Function of Column Diameter

$$a_{\text{actual}} = 0.0641(10)^{3.61/D_c} a_{\text{predicted}} \quad (56)$$

The group $0.0641(10)^{3.61/D_c}$ is the estimated scale-up factor for changing column sizes.

Comparison with Predicted Cumulative Growth of Seeds

It would be interesting to compare the cumulative growth of particles containing seeds as predicted by equation (26) by Griffin, et al.⁽²⁰⁾ with the data in this work. In deriving equation (26), only the validity of

$$D = D_o + a\theta_F \quad (25)$$

and a decay-type equation for the removal of seed particles

$$\frac{dX}{d\theta_F} = -\lambda X$$

were needed. Since the validity of equation (25) has been already established and the decay equation is physically descriptive, the cumulative growth equation (26) is expected to hold. To check this, data from Run PS-19 are used to calculate $\frac{W_{SB}}{W_{So}}$, the weight of seed-containing particles per unit weight of seeds, as a function of time and the results compared with the curve predicted from equation (26).

For a run in which initially seeds of weight W_{So} and diameter D_o having activity of A_o are added to the system, the weight of seed particles $W_{S_{ij}}$ present in the i^{th} sieve fraction of the j^{th} product sample is given by

$$W_{S_{ij}} = \left(\frac{A_i W_i}{A_o} \right)_j$$

On the i^{th} sieve having particles of diameter D_i , the weight of particles that contain seeds is

$$W_{SB_{ij}} = \left[\frac{A_i w_i \left(\frac{D_i}{D_o} \right)^3}{A_o} \right]_j$$

The sum of these seed-containing particles on each screen is the weight of "grown" seed particles in the j^{th} product:

$$W_{SB_j} = \left[\frac{1}{A_o} \sum_i A_i w_i \left(\frac{D_i}{D_o} \right)^3 \right]_j$$

From this, the weight of "grown" seed particles in the j^{th} sample per unit weight of seeds is calculated from

$$\left(\frac{W_{SB}}{W_{So}} \right)_j = \left[\frac{1}{A_o W_{So}} \sum_i A_i w_i \left(\frac{D_i}{D_o} \right)^3 \right]_j$$

From each product sample withdrawn at successive time intervals,

$\left(\frac{W_{SB}}{W_{So}} \right)_j$ is calculated. Then the total weight of "grown" seed particles withdrawn in successive samples from 1 through k is given by

$$\sum_{j=1}^{j=k} \left(\frac{W_{SB}}{W_{So}} \right)_j$$

In this manner, the data from PS-19 are analyzed and the results plotted as the "experimental" curve in Figure 11. To calculate the theoretical curve from equation (26), values of α' = ratio of weight rate of product withdrawal to the total weight of the bed, and $\sigma'/\alpha' = \frac{a}{\alpha' D_o}$ are required, where a is the overall growth constant. Using the value of a previously calculated, and for given D_o and α' , the "theoretical" curve

Figure 11. Comparison of Calculated and Predicted Cumulative Growth Curves for Seed Particles for Run PS-19

with $\alpha' = 0.098$, $\sigma'/\alpha' = 1.0$ is plotted in Figure 11. For comparison and to show the sensitivity of the predicted curve, another curve with $\sigma'/\alpha' = 0.8$ is plotted. Figure 11 indicates that the agreement between predicted and actual values is quite good. Since the data bear out the relationship of equation (26) then equation (27), derived directly from it, should hold. So the steady-state distribution of particles can be predicted from equation (27):

weight per cent of particles in steady-state mixture having
a diameter of D or less

$$\begin{aligned}
 = 100 - & \frac{100}{(1+Q)\exp \left[\left(\frac{D}{D_0} - 1 \right) / \left(\frac{\sigma'}{\alpha'} \right) \right]} \left[\left(\frac{D}{D_0} - 1 \right)^3 + 3 \left(\frac{\sigma'}{\alpha'} + 1 \right) \left(\frac{D}{D_0} - 1 \right)^2 \right. \\
 & \left. + \frac{Q}{\left(\frac{\sigma'}{\alpha'} \right)} \left(\frac{D}{D_0} - 1 \right) + 1 + Q \right] \quad (27)
 \end{aligned}$$

VII. CONCLUSIONS

It has been demonstrated in this investigation that radioactive tracer can be employed to successfully follow the mechanism of particle growth in a fluidized calciner. The hypothesis that the rate of growth of a particle is proportional to its surface area is substantiated by the extremely strong linear correlation between particle diameter and time. Good reproducibility of the data is obtained.

Of the two major factors contributing to overall growth studied in this work, it has been found that attrition due mainly to the atomizing air exerts a non-significant effect compared to normal growth. Hence, in this study, overall particle growth is essentially identical to normal growth. The influence of operating variables and physical properties of the system has been investigated with the result that the feed to bed weight ratio and the atomizing air to feed ratio are found to be of prime importance. The normal growth coefficient is related to the variables studied through the following equation:

$$K = \frac{9.83 \times 10^3 \left(\frac{F}{W}\right)^{1.25} B^{-0.467} V^{-0.147} \mu^{0.0628} \sigma^{-0.321} V_s' (1-\epsilon)}{bW}.$$

$$\left[1 - \frac{\rho_{s(1-\epsilon)}}{\rho_{bs}} \right]$$

The results from this study are compared with those obtained from larger units at the Argonne National Laboratory and at the Idaho Chemical Reprocessing Plant with the consequence that under similar operating conditions a scale-up factor due to difference in column sizes to be applied to the predicted overall growth constant is estimated, namely, $0.0641(10)^{3.61/D_c}$.

It has also been shown that the steady-state distribution of particle size can be predicted by the equation developed by Griffin, et al.⁽²⁰⁾ if jet or target attrition data are available.

VIII. APPENDIX

Review of Literature on Spray Drying, Drying, and Fluidization

Photographs of Experimental Equipment

Summary of Preliminary Work

Summary of Experimental Data and Curve Fitting

Derivation of Equation for Volume of Spray Cone

Review of Literature on Spray Drying, Drying, and Fluidization

In the monograph by Marshall⁽⁴⁰⁾ topics ranging from the mechanisms of jet break-up, performance characteristics of the various types of atomizers, and mathematical and experimental drop-size distribution to the theory of evaporation from drops and sprays were included. Fraser and Eisenklam⁽¹⁵⁾ surveyed the influence of atomizer design, liquid property, and ambient pressure on the drop size of sprays. Buckham and Moulton⁽⁴⁾ studied the effect of operating variables on the spray drying of aqueous ammonium sulfate solution, and found the drying operation depended on size and size distribution of the spray droplets, the drying gas temperature, and feed concentration. Various types of atomizers were shown to affect the spray droplet size and distribution^(1,25,60).

Little work has been published on the heat and mass transfer in spray-drying liquid solution, although Marshall^(40,41) discussed the basic equations involved. However, the solution of these equations only extended to drying from pure liquid droplets and not to droplets containing dissolved solids. In the case of the latter, making certain assumptions, an approximate solution during the constant-rate drying period could be obtained. But no method was available to describe the conditions during the falling-rate period.

Since literature on the mechanisms of spray drying was limited, the scope of the survey was expanded to include the related field of drying as well. Ranz and Marshall⁽⁵³⁾ studied primarily evaporation of single drops of pure liquid in air as well as some work on drops containing dissolved or suspended solids. The latter only provided some qualitative results. Lebeis and Burtis⁽³⁵⁾ investigated the effect of drying conditions on drying rate and physical properties of a porous solid during

both the constant-rate and falling-rate periods. Again, only qualitative conclusions were drawn. Papers by Polonskaya⁽⁵²⁾ and Heertjes and Ringens⁽²⁴⁾ treated the constant-rate period empirically. Other papers were available that tackled the problem from the theoretical standpoint. Newman⁽⁴⁹⁾ approached the drying problem assuming a diffusional mechanism but Hougen, et al.⁽²⁶⁾ presented the limitations of diffusion equations and Ceaglske and Hougen⁽⁷⁾ proposed that capillary forces governed the drying mechanism. This concept was supported by the results of van Krevelen and Hoftijzer⁽⁶¹⁾, and Corben and Newitt⁽⁹⁾. King and Newitt⁽³⁴⁾, and Butler and Plews⁽⁵⁾ also presented theoretical studies on this subject.

The existing literature on fluidization is voluminous. Efforts were directed toward the more recent researches, with special attention given to gas-solid contact characteristics. Background and basic concepts of fluidization were discussed in a number of sources^(10,14,16,50,51,59,66,67): Studies of the fundamentals of fluidization included the early work of Wilhelm and Kwauk⁽⁶⁴⁾ who correlated pressure drop, voidage fraction, and fluidizing velocity for uniform spherical particles. Later Matheson, et al.⁽⁴²⁾ studied the effect of density and viscosity on fluidized systems. Kalbach^(31,32) considered chemical reactions such as lime calcination and coal gasification in fluidized beds. Measurements of porosity conducted recently⁽²⁾ showed the assumption of constant porosity throughout the bed to be incorrect. Instead, three regions of porosity were postulated. A new method for analyzing fluidization quality by using X-ray absorption was reported⁽²³⁾. Analogies between fluidized systems and liquid systems were reported^(19,44) and can be substantiated by viscosity, surface tension, and miscibility measurements.

Completely theoretical analyses were made by Friedlander⁽¹⁷⁾, and Friedlander and Johnstone⁽¹⁸⁾ of the behavior of suspended particles in

a turbulent stream. Johnstone and Shen⁽²⁸⁾ investigated gas-solid contact in two-phase fluidized beds. A mass transfer coefficient between the two phases may be used to evaluate the effectiveness of contact between the gas and the solid.

For practical applications, coal desulfurization in a fluidized carbonizer⁽²⁷⁾ and fluid coking in a mechanically fluidized reactor⁽¹⁷⁾ were reported. A new technique for "fluidizing" wheat also was reported by a "spouting bed" method which made possible contacting gases with coarse solid particles⁽⁴³⁾.

Photographs of Experimental Equipment

Figure 12. Front View of the Three-inch Fluidized Calciner and Auxiliary Equipment

Figure 13. Side View of the Three-inch Fluidized Calciner and Auxiliary Equipment

Figure 14. Filter and Blowback Assembly for the Three-inch Fluidized Calciner

Figure 15. Components of the Spray Nozzle Used in Calcination Work

Figure 16. Spray Nozzle in Assembled Form

Figure 17 Product Withdrawal Assembly for the Three-inch Fluidized Calciner

Preliminary Work

From previous runs made with uranyl nitrate⁽³⁰⁾, it was found that the agglomeration effect was considerable. This was possibly due to the fact that uranyl nitrate had a low melting point, around 60°C. Since the bed was operated in the neighborhood of 300°C, agglomeration might be the result of particles being sintered together. To eliminate agglomeration from this study, a material of high melting point, sodium carbonate, was chosen. Sodium carbonate melts at around 850°C and is quite soluble in water. Also, it does not decompose chemically in the temperature range studied, around 300°C, as does uranyl nitrate. Thus, drying could be studied independently of chemical reaction.

Microscopic examination of dried particles from zirconium-uranium-fluoride runs in the 6-inch pilot plant column (particles furnished by J. Barghusen, Jr. of Argonne) showed a concentric ring-like structure. If the thickness of successive rings could be reliably measured, then it would be possible to estimate the particle residence time in the spray zone, the amount of feed picked up, and the circulation rate in the bed. It was hoped, therefore, that runs made with sodium carbonate particles would yield products with this ring-like structure. However, no such phenomenon was observed from the products in Runs SC-1 through SC-6.

Next, it was thought that by alternately introducing two feed streams, one colored with a dye and the other plain, rings of different colors might show up that had not been observable in the previous set of runs. First, sodium dichromate, strongly yellow, was used as dye in sodium carbonate feed solution. This stream was alternated with plain sodium carbonate solution. Later, potassium permanganate with its intense purple color was used in place of sodium dichromate. Runs SC-7 through SC-14, lasting around six hours each, failed to show any rings of growth.

Instead of alternate layers of different colors, a uniform brown (due to permanganate decomposition) color was observed.

Then, a series of runs at temperatures below the decomposition point of permanganate to preserve its deep purple color was made. These were of short durations lasting about five minutes, the purpose being not to coat all the particles in the bed. In this way, the amount of coating on the coated particles would on the average be due to a single pass through the spray zone. The expected pink-red permanganate color was observed on the coated particles but the coloring was diffuse and pale. Upon mounting these particles in Lucite, sectioning them, and examining microscopically, no growth structure was perceptible. It was believed that the diffuseness of color might be caused by the spreading of feed on the water-soluble sodium carbonate. To overcome this, a water-insoluble material, the final bed material from ZCP-38 (uranium-zirconium fluid-bed dryer product furnished by J. Barghusen, Jr.) was used in Run SC-20. However, although the coloring was much more distinct, the coating was not uniform but appeared in streaks and spots. Use of very concentrated permanganate solution still failed to show any observable ring structure in growth. It was then decided that the increase in diameter of a particle per pass through the spray zone was so small that it could not be detected visually, and the colorimetric approach was abandoned.

Next, the introduction of radioactive tracer in the feed stream was contemplated as a possible means to measure the visually non-observable growth in particle per pass through the spray zone. It was planned to inject small quantities of "spiked" feed into the column. Copper-64 was considered as a workable tracer. However, the delicate injection system required made this idea unfeasible.

Attempts were then made to use chemical seeds to trace growth. Cadmium chloride, capable of being detected in minute concentrations, was proposed as seeds in a sodium chloride bed. However, in Runs PS-1 through PS-11, it was found that sodium chloride feed solution, for reasons unknown, invariably plugged the air annulus in a very short time. Consequently, this scheme was abandoned also.

Finally, aluminum nitrate solution was used and gave satisfactory operation. Even though chemical decomposition was involved, no operational trouble was encountered, but it was difficult to find a chemical seed that would be readily analyzable in the presence of aluminum oxide (discussions with L. Ross and R. Meyer of the Analytical Section at Argonne). Consequently, radioactive aluminum oxide particles as seeds were tested and later found to be satisfactory for following the growth mechanism.

Summary of Fitting to a Least-Square Linear Correlation the Average
Diameter of Particles Containing Seeds as a Function of Time

Let x = time in hours, D_{vs} = the volume-surface mean diameter discussed in the Analysis of Data section in inches, and D_{vs}^* = diameter predicted by a least-square linear correlation. In the following calculations, $y = 10^2 D_{vs}$, $Y = 10^2 D_{vs}^*$, and x = time in hours. The relationship sought is

$$Y = a + b(x - \bar{x})$$

where $\bar{x}$ is the arithmetic mean of x . The constants a and b are given by the following expressions

$$a = \frac{1}{n_i} \sum_{i=1}^{n_i} y_i = \bar{y}$$

$$b = \frac{\sum_{i=1}^{n_i} x_i y_i - \frac{1}{n_i} \left(\sum_{i=1}^{n_i} x_i \right) \left(\sum_{i=1}^{n_i} y_i \right)}{\sum_{i=1}^{n_i} x_i^2 - \frac{1}{n_i} \left(\sum_{i=1}^{n_i} x_i \right)^2}$$

where $\bar{y}$ = arithmetic mean of y

n_i = number of data points.

After calculating a and b , in order to estimate the degree of correlation, the following two terms are calculated:

$$\sum_{i=1}^{n_i} (y_i - \bar{y})^2$$

$$\sum_{i=1}^{n_i} (y_i - \bar{y})^2$$

Then, as indication of the degree of correlation, the correlation coefficient

r and the statistic F are determined as:

$$r^2 = \frac{\sum_{i=1}^{n_i} (y_i - \bar{y})^2 - \sum_{i=1}^{n_i} (Y_i - y_i)^2}{\sum_{i=1}^{n_i} (y_i - \bar{y})^2}$$

$$F = \frac{s_p^2(y_i)}{s_e^2(y_i)}$$

where

$$s_p^2(y_i) = \frac{\sum_{i=1}^{n_i} (y_i - \bar{y})^2}{n_i - 1}$$

$$s_e^2(y_i) = \frac{\sum_{i=1}^{n_i} (Y_i - y_i)^2}{n_i - 2}$$

Finally, to estimate the precision of the determination of b, the term $s_e^2(b)$ is calculated:

$$s_e^2(b) = \frac{s_e^2(y_i)}{\sum_{i=1}^{n_i} (x_i - \bar{x})^2}$$

Then the square root $s_e^2(b)$ gives the estimated precision of b. So b is expressed as

$$b \pm s_e(b)$$

PS-14

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
.5	-5.25	.755	.672	-.083	-.279
1	-4.75	.759	.707	-.052	-.275
1.5	-4.25	.751	.741	-.010	-.283
2	-3.75	.761	.776	.015	-.273
2.5	-3.25	.808	.810	.002	-.226
3	-2.75	.820	.845	.025	-.214
3.5	-2.25	.863	.879	.016	-.171
4	-1.75	.888	.914	.026	-.146
4.5	-1.25	.919	.948	.029	-.115
5	-0.75	.930	.982	.052	-.104
5.5	-0.25	.962	1.017	.055	-.072
6	+0.25	.983	1.051	.068	-.051
6.5	0.75	.985	1.086	.101	-.049
7	1.25	1.182	1.120	-.062	.148
7.5	1.75	1.200	1.155	-.045	.166
8	2.25	1.220	1.189	-.031	.186
8.5	2.75	1.260	1.224	-.036	.226
9	3.25	1.295	1.258	-.037	.261
9.5	3.75	1.320	1.292	-.028	.286
10	4.25	1.350	1.327	-.023	.316
10.5	4.75	1.364	1.361	-.003	.330
11	5.25	1.368	1.396	.028	.334

$$\sum x_i = 126.5$$

$$\sum (Y_i - y_i)^2 = 0.044475$$

$$\bar{x} = 5.75$$

$$\sum (y_i - \bar{y})^2 = 1.095101$$

$$\sum x_i^2 = 948.75$$

$$\sum (x_i - \bar{x})^2 = 221.375$$

$$\frac{1}{n} (\sum x_i)^2 = 727.38$$

$$s_p^2(y_i) = 0.052147$$

$$\sum y_i = 22.743$$

$$s_e^2(y_i) = 0.0022238$$

$$\bar{y} = a = 1.034$$

$$r^2 = 0.959, r = 0.980$$

$$\sum x_i y_i = 146.024$$

$$F = 23.45$$

$$\frac{1}{n} (\sum x_i)(\sum y_i) = 130.772$$

$$s_e^2(b) = 10.0454 \times 10^{-6}$$

$$b = 0.06890$$

$$s_e(b) = \pm 0.00317$$

$$Y = 0.638 + 0.0689x$$

$$b = 0.06890 \pm 0.00317$$

PS-19

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
0.5	-10.5	0.820	0.788	-0.032	-0.691
1.0	-10.0	0.885	0.823	-0.062	-0.626
1.5	- 9.5	0.872	0.857	-0.015	-0.639
2.0	- 9.0	0.940	0.892	-0.048	-0.571
2.5	- 8.5	0.963	0.926	-0.037	-0.548
3.0	- 8.0	1.035	0.960	-0.075	-0.476
3.5	- 7.5	1.026	0.995	-0.031	-0.485
4.0	- 7.0	1.032	1.029	-0.003	-0.479
4.5	- 6.5	1.040	1.064	0.024	-0.471
5.0	- 6.0	1.050	1.098	0.048	-0.461
5.5	- 5.5	1.052	1.132	0.080	-0.459
6.0	- 5.0	1.058	1.167	0.109	-0.453
6.5	- 4.5	1.089	1.201	0.112	-0.422
7.0	- 4.0	1.183	1.236	0.053	-0.328
7.5	- 3.5	1.290	1.270	-0.020	-0.221
8.0	- 3.0	1.287	1.305	0.018	-0.224
8.5	- 2.5	1.350	1.339	-0.011	-0.161
9.0	- 2.0	1.370	1.373	0.003	-0.141
9.5	- 1.5	1.400	1.408	0.008	-0.111
10.0	- 1.0	1.426	1.442	0.016	-0.085
10.5	- 0.5	1.445	1.477	0.032	-0.066
11.0	0	1.462	1.511	0.049	-0.049
11.5	0.5	1.520	1.546	0.026	0.009
12.0	1.0	1.515	1.580	0.065	0.004
12.5	1.5	1.574	1.614	0.040	0.063
13.0	2.0	1.598	1.649	0.051	0.087
13.5	2.5	1.678	1.683	0.005	0.167
14.0	3.0	1.770	1.718	-0.052	0.259
14.5	3.5	1.823	1.752	-0.071	0.312
15.0	4.0	1.875	1.786	-0.089	0.364
15.5	4.5	1.950	1.821	-0.129	0.439
16.0	5.0	2.000	1.855	-0.145	0.489
16.5	5.5	2.000	1.890	-0.110	0.489
17.0	6.0	2.01	1.924	-0.086	0.499
17.5	6.5	2.00	1.959	-0.041	0.489
18.0	7.0	1.983	1.993	0.010	0.472
18.5	7.5	1.987	2.028	0.041	0.476
19.0	8.0	1.992	2.062	0.070	0.481
19.5	8.5	2.02	2.096	0.076	0.509
20.0	9.0	2.05	2.131	0.081	0.539
20.5	9.5	2.10	2.165	0.065	0.589
21.0	10.0	2.19	2.200	0.001	0.679
21.5	10.5	2.27	2.234	-0.036	0.759

$$\sum x_i = 473.0$$

$$\bar{x} = 11.0$$

$$\sum x_i^2 = 6858.5$$

$$\frac{1}{n_i} (\sum x_i)^2 = 5203$$

$$\sum y_i = 64.980$$

$$\bar{y} = a = 1.511$$

$$\sum x_i y_i = 828.76$$

$$\frac{1}{n_i} (\sum x_i)(\sum y_i) = 714.78$$

$$b = 0.06885$$

$$Y = 0.754 + 0.06885x$$

$$\sum (Y_i - y_i)^2 = 0.16465$$

$$\sum (y_i - \bar{y})^2 = 8.0122$$

$$\sum (x_i - \bar{x})^2 = 1655.5$$

$$s_p^2(y_i) = 0.19077$$

$$s_e^2(y_i) = 0.0040158$$

$$r^2 = 0.980, r = 0.991$$

$$F = 47.50$$

$$s_e^2(b) = 2.4257 \times 10^{-6}$$

$$s_e(b) = \pm 0.00156$$

$$b = 0.06885 \pm 0.00156$$

PS-20

x_1	$x_1 - \bar{x}$	y_1	Y_1	$Y_1 - y_1$	$y_1 - \bar{y}$
.5	-7.0	.970	.909	-.061	-.433
1.5	-6.0	.980	.980	=	-.423
2.5	-5.0	.941	1.050	.109	-.462
3.5	-4.0	1.090	1.121	.031	-.313
4.5	-3.0	1.192	1.192	=	-.211
5.5	-2.0	1.332	1.262	-.070	-.071
6.5	-1.0	1.384	1.333	-.051	-.019
7.5	0	1.400	1.403	.003	-.003
8.5	1.0	1.551	1.474	-.077	.148
9.5	2.0	1.543	1.544	.001	.140
10.5	3.0	1.560	1.615	.055	.157
11.5	4.0	1.500	1.685	.185	.097
12.5	5.0	1.757	1.756	-.001	.354
13.5	6.0	1.888	1.826	-.062	.485
14.5	7.0	1.955	1.897	-.058	.552

$$\sum x_1 = 112.5$$

$$\bar{x} = 7.5$$

$$\sum x_1^2 = 1123.75$$

$$\frac{1}{n_1} (\sum x_1)^2 = 843.75$$

$$\sum y_1 = 21.043$$

$$\bar{y} = a = 1.403$$

$$\sum x_1 y_1 = 177.5785$$

$$\frac{1}{n_1} (\sum x_1)(\sum y_1) = 157.8225$$

$$b = 0.07055$$

$$Y = 0.874 + 0.07055x$$

$$\sum (Y_1 - y_1)^2 = 0.074462$$

$$\sum (y_1 - \bar{y})^2 = 1.468570$$

$$\sum (x_1 - \bar{x})^2 = 280$$

$$s_p^2(y_1) = 0.10489$$

$$s_e^2(y_1) = 0.0057278$$

$$r^2 = 0.949, r = 0.975$$

$$F = 18.31$$

$$s_e^2(b) = 20.46 \times 10^{-6}$$

$$s_e(b) = \pm 0.00453$$

$$b = 0.07055 \pm 0.00453$$

PS-26

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
0.5	-7.75	0.900	0.895	-0.005	-0.556
1	-7.25	.957	.931	-0.026	-0.499
1.5	-6.75	.997	.967	-0.030	-0.459
2	-6.25	1.020	1.003	-0.017	-.436
2.5	-5.75	1.052	1.040	-0.012	-.404
3	-5.25	1.080	1.076	-0.004	-.376
3.5	-4.75	1.113	1.112	-0.001	-.343
4	-4.25	1.143	1.148	.005	-.313
4.5	-3.75	1.170	1.184	.014	-.286
5	-3.25	1.200	1.221	.021	-.256
5.5	-2.75	1.231	1.257	.026	-.225
6	-2.25	1.262	1.293	.031	-.194
6.5	-1.75	1.296	1.330	.004	-.160
7	-1.25	1.332	1.366	.034	-.124
7.5	-0.75	1.363	1.402	.039	-.093
8	-0.25	1.385	1.438	.053	-.071
8.5	.25	1.385	1.474	.089	-.071
9	.75	1.553	1.511	-.042	.097
9.5	1.25	1.589	1.547	-.042	.133
10	1.75	1.632	1.583	-.049	.176
10.5	2.25	1.663	1.619	-.044	.207
11	2.75	1.687	1.656	-.031	.231
11.5	3.25	1.720	1.692	-.028	.264
12	3.75	1.747	1.728	-.019	.291
12.5	4.25	1.800	1.764	-.036	.344
13	4.75	1.845	1.801	-.044	.389
13.5	5.25	1.860	1.837	-.023	.404
14	5.75	1.857	1.873	.016	.401
14.5	6.25	1.912	1.909	-.003	.456
15	6.75	1.941	1.946	.005	.485
15.5	7.25	1.960	1.982	.022	.504
16	7.75	1.952	2.018	.066	.496

$$\sum x_i = 264$$

$$\bar{x} = 8.25$$

$$\sum x_i^2 = 2860$$

$$\frac{1}{n_i} (\sum x_i)^2 = 2178$$

$$\sum y_i = 46.604$$

$$\bar{y} = a = 1.4564$$

$$\sum x_i y_i = 433.9095$$

$$\frac{1}{n_i} (\sum x_i)(\sum y_i) = 384.48$$

$$b = 0.07248$$

$$Y = 0.858 + 0.07248x$$

$$\sum (Y_i - y_i)^2 = 0.036635$$

$$\sum (y_i - \bar{y})^2 = 3.619952$$

$$\sum (x_i - \bar{x})^2 = 3657.5$$

PS-26 continued

$$s_p^2(y_i) = 0.11677$$

$$s_e^2(y_i) = 0.0012211$$

$$r^2 = 0.990, r = 0.996$$

$$F = 95.62$$

$$s_e^2(b) = 33.4 \times 10^{-8}$$

$$s_e(b) = \pm 0.00058$$

$$b = 0.07248 \pm 0.00058$$

PS-45

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
0	-7.5	.788	.775	-.013	-.491
1	-6.5	.922	.842	-.080	-.357
2	-5.5	.979	.910	-.069	-.300
3	-4.5	1.012	.977	-.035	-.267
4	-3.5	1.017	1.044	.027	-.262
5	-2.5	1.011	1.111	.100	-.268
6	-1.5	1.015	1.178	.163	-.264
7	-0.5	1.344	1.246	-.098	.065
8	0.5	1.329	1.313	-.016	.050
9	1.5	1.356	1.380	.024	.077
10	2.5	1.383	1.448	.065	.104
11	3.5	1.555	1.515	-.040	.276
12	4.5	1.510	1.582	.072	.231
13	5.5	1.545	1.649	.104	.266
14	6.5	1.720	1.716	-.004	.441
15	7.5	1.980	1.784	-.196	.701

$$\sum x_i = 120$$

$$\bar{x} = 7.5$$

$$\sum x_i^2 = 1239$$

$$\frac{1}{n_i} (\sum x_i)^2 = 900$$

$$\sum y_i = 20.466$$

$$\bar{y} = a = 1.279$$

$$\sum x_i y_i = 176.293$$

$$\frac{1}{n_i} (\sum x_i)(\sum y_i) = 153.495$$

$$b = 0.06725$$

$$Y = 0.775 + 0.06725x$$

$$\sum (Y_i - y_i)^2 = 0.120546$$

$$\sum (y_i - \bar{y})^2 = 1.649628$$

$$\sum (x_i - \bar{x})^2 = 340$$

$$s_p^2(y_i) = 0.109975$$

$$s_e^2(y_i) = 0.0086104$$

$$r^2 = 0.927, r = 0.964$$

$$F = 12.77$$

$$s_e^2(b) = 25.3 \times 10^{-6}$$

$$s_e(b) = \pm 0.00504$$

$$b = 0.06725 \pm 0.00504$$

PS-46

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
0	-1.0	.765	.769	.004	-.146
.5	-0.5	.815	.840	.025	-.096
1.0	0	.958	.911	.047	.047
1.5	0.5	.977	.983	.006	.066
2	1.0	1.040	1.054	.014	.129

$$\sum x_i = 5$$

$$\bar{x} = 1$$

$$\sum x_i^2 = 7.5$$

$$\frac{1}{n_i} (\sum x_i)^2 = 5$$

$$\sum y_i = 4.555$$

$$\bar{y} = a = 0.911$$

$$\sum x_i y_i = 4.911$$

$$\frac{1}{n_i} (\sum x_i)(\sum y_i) = 4.555$$

$$b = 0.1424$$

$$Y = 0.769 + 0.1424x$$

$$\sum (Y_i - y_i)^2 = 0.003082$$

$$\sum (y_i - \bar{y})^2 = 0.053738$$

$$\sum (x_i - \bar{x})^2 = 2.50$$

$$s_p^2(y_i) = 0.013434$$

$$s_e^2(y_i) = 0.001027$$

$$r^2 = 0.943, r = 0.973$$

$$F = 13.08$$

$$s_e^2(b) = 4.108 \times 10^{-4}$$

$$s_e(b) = \pm 0.0207$$

$$b = 0.1424 \pm 0.0207$$

PS-49

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
1	-11.5	1.032	0.991	-0.041	-.348
2	-10.5	1.020	1.025	.005	-.360
3	- 9.5	1.078	1.058	- .020	-.302
4	- 8.5	1.121	1.092	- .029	-.259
5	- 7.5	1.122	1.126	.004	-.258
6	- 6.5	1.143	1.160	.017	-.237
7	- 5.5	1.142	1.194	.052	-.238
8	- 4.5	1.225	1.228	.003	-.155
9	- 3.5	1.240	1.261	.021	-.140
10	- 2.5	1.188	1.295	.107	-.192
11	- 1.5	1.272	1.329	.057	-.108
12	- 0.5	1.364	1.363	-.001	-.016
13	0.5	1.435	1.397	-.038	+.055
14	1.5	1.490	1.430	-.060	.110
15	2.5	1.453	1.464	.011	.073
16	3.5	1.468	1.498	.030	.088
17	4.5	1.557	1.532	-.025	.187
18	5.5	1.531	1.566	.035	.151
19	6.5	1.630	1.600	-.030	.250
20	7.5	1.597	1.633	.036	.217
21	8.5	1.667	1.667	-	.287
22	9.5	1.701	1.701	-	.321
23	10.5	1.787	1.735	-.052	.407
24	11.5	1.858	1.769	.089	.478

$$\sum x_i = 300$$

$$\bar{x} = 12.5$$

$$\sum x_i^2 = 4900$$

$$\frac{1}{n_1} (\sum x_i)^2 = 3750$$

$$\sum y_i = 33.121$$

$$\bar{y} = a = 1.380$$

$$\sum x_i y_i = 452.903$$

$$\frac{1}{n_1} (\sum x_i)(\sum y_i) = 414.012$$

$$b = 0.03382$$

$$Y = 0.957 + 0.03382x$$

$$\sum (Y_i - y_i)^2 = 0.041841$$

$$\sum (y_i - \bar{y})^2 = 1.455875$$

$$\sum (x_i - \bar{x})^2 = 1150$$

$$s_p^2(y_i) = 0.06329$$

$$s_e^2(y_i) = 0.0019018$$

$$r^2 = 0.971, r = 0.986$$

$$F = 33.28$$

$$s_e^2(b) = 1.654 \times 10^{-6}$$

$$s_e(b) = \pm 0.00129$$

$$b = 0.03382 \pm 0.00129$$

PS-50

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
1	-11.48	1.057	1.077	.020	-.364
2	-10.48	1.030	1.107	.077	-.391
3	- 9.48	1.143	1.137	-.006	-.278
4	- 8.48	1.170	1.167	-.003	-.251
5	- 7.48	1.208	1.197	-.011	-.213
6	- 6.48	1.216	1.227	.011	-.205
7	- 5.48	1.286	1.257	-.029	-.135
8	- 4.48	1.304	1.287	-.017	-.117
9	- 3.48	1.212	1.317	.105	-.209
10	- 2.48	1.411	1.347	-.064	-.010
11	- 1.48	1.464	1.377	-.087	.043
12	- 0.48	1.567	1.407	-.160	.146
14	1.52	1.437	1.467	.030	.016
15	2.52	1.492	1.497	.005	.071
16	3.52	1.453	1.527	.074	.032
17	4.52	1.610	1.557	-.053	.189
18	5.52	1.583	1.587	.004	.162
19	6.52	1.567	1.617	.050	.146
20	7.52	1.590	1.647	.057	.169
21	8.52	1.647	1.677	.030	.226
22	9.52	1.697	1.707	.010	.276
23	10.52	1.765	1.737	-.028	.344
24	11.52	1.785	1.767	-.018	.364

$$\sum x_i = 287$$

$$\bar{x} = 12.48$$

$$\sum x_i^2 = 4731$$

$$\frac{1}{n_1} (\sum x_i)^2 = 3581.2$$

$$\sum y_i = 32.694$$

$$\bar{y} = a = 1.4214$$

$$\sum x_i y_i = 442.46$$

$$\frac{1}{n_1} (\sum x_i)(\sum y_i) = 407.96$$

$$b = 0.03000$$

$$Y = 1.047 + 0.03000x$$

$$\sum (Y_i - y_i)^2 = 0.073119$$

$$\sum (y_i - \bar{y})^2 = 1.108163$$

$$\sum (x_i - \bar{x})^2 = 1149.739$$

$$s_p^2(y_i) = 0.05037$$

$$s_e^2(y_i) = 0.003482$$

$$r^2 = 0.931, r = 0.966$$

$$F = 14.46$$

$$s_e^2(b) = 3.028 \times 10^{-6}$$

$$s_e(b) = \pm 0.00174$$

$$b = 0.03000 \pm 0.00174$$

PS-53

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
0.5	-5.21	1.011	.982	-.029	-.169
1.0	-4.71	1.001	1.001	-	-.179
1.5	-4.21	1.022	1.020	-.002	-.158
2	-3.71	1.071	1.039	-.032	-.109
3	-2.71	1.038	1.077	.039	-.142
4	-1.71	1.051	1.115	.064	-.129
5	-0.71	1.094	1.153	.059	-.086
6	0.29	1.252	1.190	-.062	+.072
7	1.29	1.223	1.228	.005	.043
8	2.29	1.285	1.266	-.019	.105
9	3.29	1.379	1.304	-.075	.199
10	4.29	1.374	1.342	-.032	.194
11	5.29	1.286	1.380	.094	.106
12	6.29	1.429	1.417	-.012	.249

$$\sum x_i = 80$$

$$\bar{x} = 5.71$$

$$\sum x_i^2 = 652.5$$

$$\frac{1}{n_1} (\sum x_i)^2 = 457.1$$

$$\sum y_i = 16.516$$

$$\bar{y} = a = 1.1797$$

$$\sum x_i y_i = 101.7675$$

$$\frac{1}{n_1} (\sum x_i)(\sum y_i) = 94.377$$

$$b = 0.03782$$

$$Y = 0.964 + 0.03782x$$

$$\sum (Y_i - y_i)^2 = 0.030826$$

$$\sum (y_i - \bar{y})^2 = 0.310180$$

$$\sum (x_i - \bar{x})^2 = 195.357$$

$$s_p^2(y_i) = 0.02386$$

$$s_e^2(y_i) = 0.0025688$$

$$r^2 = 0.901, r = 0.950$$

$$F = 9.29$$

$$s_e^2(b) = 13.149 \times 10^{-6}$$

$$s_e(b) = \pm 0.00362$$

$$b = 0.03782 \pm 0.00362$$

PS-53

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
1	-11.5	1.087	1.028	-.059	-.367
2	-10.5	1.087	1.065	-.022	-.367
3	-9.5	1.094	1.102	.008	-.360
4	-8.5	1.149	1.139	-.010	-.305
5	-7.5	1.090	1.176	.086	-.364
6	-6.5	1.201	1.213	.012	-.253
7	-5.5	1.278	1.250	-.028	-.176
8	-4.5	1.282	1.287	.005	-.172
9	-3.5	1.371	1.324	-.047	-.083
10	-2.5	1.440	1.361	-.079	-.014
11	-1.5	1.255	1.398	.143	-.199
12	-0.5	1.430	1.435	.005	-.024
13	0.5	1.395	1.472	.077	-.059
14	1.5	1.610	1.509	-.101	.156
15	2.5	1.476	1.546	.070	.022
16	3.5	1.651	1.583	-.068	.197
17	4.5	1.533	1.620	.087	.079
18	5.5	1.782	1.657	-.125	.328
19	6.5	1.561	1.694	.133	.107
20	7.5	1.810	1.731	-.079	.356
21	8.5	1.685	1.768	.083	.231
22	9.5	1.930	1.805	-.125	.476
23	10.5	1.736	1.842	.106	.282
24	11.5	1.961	1.879	-.082	.507

$$\sum x_i = 300$$

$$\bar{x} = 12.5$$

$$\sum x_i^2 = 4900$$

$$\frac{1}{n_i} (\sum x_i)^2 = 3750$$

$$\sum y_i = 34.894$$

$$\bar{y} = a = 1.454$$

$$\sum x_i y_i = 478.765$$

$$\frac{1}{n_i} (\sum x_i)(\sum y_i) = 436.175$$

$$b = 0.03703$$

$$Y = 0.991 + 0.03703x$$

$$\sum (Y_i - y_i)^2 = 0.154654$$

$$\sum (y_i - \bar{y})^2 = 1.731960$$

$$\sum (x_i - \bar{x})^2 = 1150$$

$$s_p^2(y_i) = 0.075302$$

$$s_e^2(y_i) = 0.0070297$$

$$r^2 = 0.911, r = 0.955$$

$$F = 10.71$$

$$s_e^2(b) = 6.113 \times 10^{-6}$$

$$s_e(b) = \pm 0.00208$$

$$b = 0.03703 \pm 0.00248$$

PS-57

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
1	-7.5	0.871	.951	.080	-.287
2	-6.5	1.020	.979	-.041	-.138
3	-5.5	1.054	1.006	-.048	-.104
4	-4.5	1.095	1.034	-.061	-.063
5	-3.5	1.098	1.061	-.037	-.060
6	-2.5	1.088	1.089	.001	-.070
7	-1.5	1.080	1.117	.037	-.078
8	-0.5	1.133	1.144	.011	-.025
9	0.5	1.112	1.172	.060	-.046
10	1.5	1.177	1.199	.022	.019
11	2.5	1.175	1.227	.052	.017
12	3.5	1.237	1.255	.018	.079
13	4.5	1.310	1.282	-.028	.152
14	5.5	1.342	1.310	-.032	.184
15	6.5	1.363	1.337	-.026	.205
16	7.5	1.373	1.365	-.008	.215

$$\sum x_i = 136$$

$$\bar{x} = 8.50$$

$$\sum x_i^2 = 1496$$

$$\frac{1}{n_i} (\sum x_i)^2 = 1156$$

$$\sum y_i = 18.528$$

$$\bar{y} = a = 1.1580$$

$$\frac{1}{n_i} (\sum x_i)(\sum y_i) = 157.488$$

$$b = 0.02760$$

$$Y = 0.923 + 0.02760x$$

$$\sum (y_i - y_i)^2 = 0.026626$$

$$\sum (y_i - \bar{y})^2 = 0.285624$$

$$\sum (x_i - \bar{x})^2 = 340$$

$$s_p^2(y_i) = 0.019041$$

$$s_e^2(y_i) = 0.001902$$

$$r^2 = 0.907, r = 0.953$$

$$F = 10.01$$

$$s_e^2(b) = 5.594 \times 10^{-6}$$

$$s_e(b) = \pm 0.00236$$

$$b = 0.02760 \pm 0.00236$$

PS-58

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
1	-11.5	.810	0.864	.054	-.266
2	-10.5	.863	.882	.019	-.213
3	- 9.5	.992	.900	-.092	-.084
4	- 8.5	.977	.919	-.058	-.099
5	- 7.5	.992	.938	-.054	-.084
6	- 6.5	.990	.956	-.034	-.086
7	- 5.5	.995	.974	-.021	-.081
8	- 4.5	.999	.993	-.006	-.077
9	- 3.5	.997	1.012	+.015	-.079
10	- 2.5	.998	1.030	.032	-.078
11	- 1.5	1.010	1.048	.038	-.066
12	- 0.5	1.036	1.067	.031	-.040
13	0.5	1.034	1.086	.052	-.042
14	1.5	1.059	1.104	.045	-.016
15	2.5	1.085	1.122	.037	.069
16	3.5	1.082	1.141	.059	.006
17	4.5	1.127	1.160	.033	.051
18	5.5	1.175	1.178	.003	.099
19	6.5	1.192	1.196	.004	.116
20	7.5	1.210	1.215	.005	.134
21	8.5	1.250	1.234	-.016	.174
22	9.5	1.284	1.252	-.032	.208
23	10.5	1.326	1.270	-.056	.250
24	11.5	1.351	1.289	-.062	.275

$$\sum x_i = 300$$

$$\bar{x} = 12.5$$

$$\sum x_i^2 = 4900$$

$$\frac{1}{n_i} (\sum x_i)^2 = 3750$$

$$\sum y_i = 25.834$$

$$\bar{y} = a = 1.076$$

$$\sum x_i y_i = 344.204$$

$$\frac{1}{n_i} (\sum x_i)(\sum y_i) = 322.925$$

$$b = 0.01850$$

$$Y = 0.845 + 0.01850x$$

$$\sum (y_i - y_i)^2 = 0.042286$$

$$\sum (y_i - \bar{y})^2 = 0.435821$$

$$\sum (x_i - \bar{x})^2 = 1150$$

$$s_p^2(y_i) = 0.018948$$

$$s_e^2(y_i) = 0.0019220$$

$$r^2 = 0.903, r = 0.952$$

$$F = 9.86$$

$$s_e^2(b) = 1.671 \times 10^{-6}$$

$$s_e(b) = \pm 0.00129$$

$$b = 0.01850 \pm 0.00129$$

PS-59

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
1	-11.5	.898	.915	.017	-.216
2	-10.5	.881	.932	.051	-.233
3	- 9.5	.985	.950	-.035	-.129
4	- 8.5	.978	.967	-.011	-.136
5	- 7.5	.992	.984	-.008	-.122
6	- 6.5	1.040	1.002	-.038	-.074
7	- 5.5	1.038	1.019	-.019	-.076
8	- 4.5	1.014	1.036	.022	-.100
9	- 3.5	1.050	1.053	.003	-.064
10	- 2.5	1.142	1.071	-.071	.028
11	- 1.5	1.035	1.088	.053	-.079
12	- 0.5	1.123	1.105	-.018	.009
13	0.5	1.140	1.122	-.018	.026
14	1.5	1.142	1.140	-.002	.028
15	2.5	1.105	1.157	.052	.009
16	3.5	1.145	1.174	.029	.031
17	4.5	1.193	1.192	-.001	.079
18	5.5	1.192	1.209	.017	.078
19	6.5	1.212	1.226	.014	.098
20	7.5	1.230	1.243	.013	.116
21	8.5	1.258	1.261	.003	.144
22	9.5	1.317	1.278	-.039	.203
23	10.5	1.294	1.295	.001	.180
24	11.5	1.335	1.312	-.023	.221

$$\sum x_i = 300$$

$$\bar{x} = 12.5$$

$$\sum x_i^2 = 4900$$

$$\frac{1}{n_i} (\sum x_i)^2 = 3750$$

$$\sum y_i = 26.739$$

$$\bar{y} = a = 1.114$$

$$\sum x_i y_i = 354.098$$

$$\frac{1}{n_i} (\sum x_i)(\sum y_i) = 334.238$$

$$b = 0.01727$$

$$Y = 0.898 + 0.01727x$$

$$\sum (Y_i - y_i)^2 = 0.021360$$

$$\sum (y_i - \bar{y})^2 = 0.364493$$

$$\sum (x_i - \bar{x})^2 = 1150$$

$$s_p^2(y_i) = 0.0158475$$

$$s_e^2(y_i) = 0.0009709$$

$$r^2 = 0.941, r = 0.976$$

$$F = 16.32$$

$$s_e^2(b) = 0.844 \times 10^{-6}$$

$$s_e(b) = \pm 0.00092$$

$$b = 0.01727 \pm 0.00092$$

PS-60

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
1	-11.5	1.020	1.117	.097	-.418
2	-10.5	1.017	1.145	.128	-.421
3	- 9.5	1.141	1.173	.032	-.297
4	- 8.5	1.180	1.201	.021	-.258
5	- 7.5	1.305	1.229	-.076	-.133
6	- 6.5	1.266	1.257	-.009	-.172
7	- 5.5	1.314	1.285	-.029	-.124
8	- 4.5	1.325	1.313	-.012	-.113
9	- 3.5	1.405	1.340	-.065	-.033
10	- 2.5	1.385	1.368	-.017	-.053
11	- 1.5	1.436	1.396	-.040	-.002
12	- 0.5	1.492	1.424	-.068	.054
13	0.5	1.538	1.452	-.086	.100
14	1.5	1.480	1.480	-	.042
15	2.5	1.572	1.508	-.064	.134
16	3.5	1.532	1.536	.004	.094
17	4.5	1.582	1.564	-.018	.144
18	5.5	1.600	1.592	-.008	.162
19	6.5	1.607	1.620	.013	.169
20	7.5	1.618	1.648	.030	.180
21	8.5	1.652	1.676	.024	.214
22	9.5	1.680	1.704	.024	.242
23	10.5	1.638	1.732	.094	.200
24	11.5	1.733	1.760	.027	.295

$$\sum x_i = 300$$

$$\bar{x} = 12.5$$

$$\sum x_i^2 = 4900$$

$$\frac{1}{n_i} (\sum x_i)^2 = 3750$$

$$\sum y_i = 34.518$$

$$\bar{y} = a = 1.438$$

$$\sum x_i y_i = 463.622$$

$$\frac{1}{n_i} (\sum x_i)(\sum y_i) = 431.475$$

$$b = 0.02795$$

$$Y = 1.089 + 0.02795x$$

$$\sum (Y_i - y_i)^2 = 0.068520$$

$$\sum (y_i - \bar{y})^2 = 0.966856$$

$$\sum (x_i - \bar{x})^2 = 1150$$

$$s_p^2(y_i) = 0.0420372$$

$$s_e^2(y_i) = 0.00311454$$

$$r^2 = 0.929, r = 0.965$$

$$F = 13.50$$

$$s_e^2(b) = 2.7082 \times 10^{-6}$$

$$s_e(b) = \pm 0.00165$$

$$b = 0.02795 \pm 0.00165$$

PS-61

x_i	$x_i - \bar{x}$	y_i	Y_i	$Y_i - y_i$	$y_i - \bar{y}$
1	-11.5	.910	.974	.064	-.381
2	-10.5	.960	1.001	.041	-.331
3	- 9.5	1.118	1.029	-.089	-.173
4	- 8.5	1.078	1.056	-.022	-.213
5	- 7.5	1.088	1.084	-.004	-.203
6	- 6.5	1.160	1.111	-.049	-.131
7	- 5.5	1.165	1.139	-.026	-.126
8	- 4.5	1.171	1.167	-.004	-.120
9	- 3.5	1.153	1.194	.041	-.138
10	- 2.5	1.178	1.222	.044	-.113
11	- 1.5	1.221	1.249	.028	-.070
12	- 0.5	1.283	1.277	-.006	-.008
13	0.5	1.261	1.304	.043	-.030
14	1.5	1.340	1.332	-.008	.049
15	2.5	1.367	1.360	-.007	.076
16	3.5	1.408	1.387	-.021	.117
17	4.5	1.450	1.415	-.035	.159
18	5.5	1.496	1.442	-.054	.205
19	6.5	1.433	1.470	.037	.142
20	7.5	1.472	1.498	.026	.181
21	8.5	1.513	1.525	.012	.222
22	9.5	1.595	1.553	-.042	.304
23	10.5	1.560	1.580	.020	.269
24	11.5	1.599	1.608	.009	.308

$$\sum x_i = 300$$

$$\bar{x} = 12.5$$

$$\sum x_i^2 = 4900$$

$$\frac{1}{n_i} (\sum x_i)^2 = 3750$$

$$\sum y_i = 30.979$$

$$\bar{y} = a = 1.291$$

$$\sum x_i y_i = 418.953$$

$$\frac{1}{n_i} (\sum x_i)(\sum y_i) = 387.238$$

$$b = 0.02758$$

$$Y = 0.946 + 0.02758x$$

$$\sum (Y_i - y_i)^2 = 0.032706$$

$$\sum (y_i - \bar{y})^2 = 0.907365$$

$$\sum (x_i - \bar{x})^2 = 1150$$

$$s_p^2(y_i) = 0.0394506$$

$$s_e^2(y_i) = 0.0014866$$

$$r^2 = 0.964, r = 0.983$$

$$F = 26.54$$

$$s_e^2(b) = 1.2926 \times 10^{-6}$$

$$s_e(b) = \pm 0.00114$$

$$b = 0.02758 \pm 0.00114$$

Derivation of Equation for the Volume of Spray Cone in an Empty Column

Volume of the Spray Cone Intercepted at Right Angles by a Cylindrical Column:

Let R = radius of cylinder

$$\text{Equation of Cone: } x^2 + y^2 = K^2 z^2 \quad (1)$$

$$\text{Equation of Cylinder: } x^2 + (z-R)^2 = R^2 \quad (2)$$

The intersection of the cylinder and cone projected on the xy -plane is obtained by solving (1) and (2) and eliminating z

$$(2) \quad x^2 + z^2 - 2Rz = 0$$

$$(1) \quad z^2 = \frac{x^2 + y^2}{K^2}$$

So (2) becomes

$$x^2 + \frac{x^2 + y^2}{K^2} = \frac{2R}{K} \sqrt{x^2 + y^2} \quad (3)$$

In polar coordinates: $x = r \cos \theta$, $y = r \sin \theta$

Then (3) becomes

$$r \cos^2 \theta + \frac{r}{K^2} = \frac{2R}{K}$$

or

$$r = \frac{2RK}{K^2 \cos^2 \theta + 1}$$

The required volume is:

$$V_s' = 4 \int_A z(r, \theta) dA \quad \text{where } A = \text{area of one quadrant in } xy\text{-plane, since the intersection is a symmetrical one.}$$

$$V_s' = 4 \int_0^{\frac{\pi}{2}} d\theta \int_0^{\frac{2RK}{K^2 \cos^2 \theta + 1}} r dr \left[z(\text{cylinder}) - z(\text{cone}) \right] \quad (4)$$

From (2)

$$z = R \pm \sqrt{R^2 - r^2}, \text{ we take } + \text{ root since } z(\text{cylinder}) \geq R,$$

$$\text{then } z(\text{cylinder}) = R + \sqrt{R^2 - r^2 \cos^2 \theta}$$

$$z(\text{cone}) = \frac{r}{K}$$

So

$$\begin{aligned} V_s' &= 4 \int_0^{\frac{\pi}{2}} d\theta \int_0^{\frac{2RK}{K^2 \cos^2 \theta + 1}} r dr \left[R + \sqrt{R^2 - r^2 \cos^2 \theta} - \frac{r}{K} \right] \\ &= 4 \int_0^{\frac{\pi}{2}} d\theta \left[R \frac{r^2}{2} - \frac{(R^2 - r^2 \cos^2 \theta)^{3/2}}{3 \cos^2 \theta} - \frac{r^3}{3K} \right]_0^{\frac{2RK}{K^2 \cos^2 \theta + 1}} \\ &= 4R^3 \int_0^{\frac{\pi}{2}} \left[\frac{2K^2}{(K^2 \cos^2 \theta + 1)^2} - \frac{\left(1 - \frac{4K^2 \cos^2 \theta}{(K^2 \cos^2 \theta + 1)^2} \right)^{3/2}}{3 \cos^2 \theta} \right. \\ &\quad \left. - \frac{8K^2}{3(K^2 \cos^2 \theta + 1)^3} + \frac{1}{3 \cos^2 \theta} \right] d\theta \quad (5) \end{aligned}$$

Now

$$\left[1 - \frac{4K^2 \cos^2 \theta}{(K^2 \cos^2 \theta + 1)^2} \right]^{3/2} = \left[\frac{(K^2 \cos^2 \theta - 1)^2}{(K^2 \cos^2 \theta + 1)^2} \right]^{3/2}$$

$$= - \left(\frac{K^2 \cos^2 \theta - 1}{K^2 \cos^2 \theta + 1} \right)^3$$

Note we take the negative square root because as $\cos \theta \rightarrow 0$, the terms in brackets $\rightarrow +1$, but the terms in parentheses $\rightarrow -1$.

We simplify the integral of (5), so that

$$V_s' = 4R^3 \int_0^{\frac{\pi}{2}} \frac{2K^2(K^2 \cos^2 \theta + 2)}{3(K^2 \cos^2 \theta + 1)^2} d\theta$$

Using the method of partial fractions, we obtain

$$V_s' = \frac{8K^2 R^3}{3} \left[\int_0^{\frac{\pi}{2}} \frac{d\theta}{(K^2 \cos^2 \theta + 1)} + \int_0^{\frac{\pi}{2}} \frac{d\theta}{(K^2 \cos^2 \theta + 1)^2} \right]$$

The first integral, by Peirce formula 315, is

$$\int_0^{\frac{\pi}{2}} \frac{d\theta}{(K^2 \cos^2 \theta + 1)} = \frac{\pi}{2} \frac{1}{\sqrt{K^2 + 1}}$$

The second integral must be further broken down:

$$\frac{1}{(K^2 \cos^2 \theta + 1)^2} = \frac{1}{K^4 \left(\sin \theta + \sqrt{\frac{K^2 + 1}{K^2}} \right)^2 \left(\sin \theta - \sqrt{\frac{K^2 + 1}{K^2}} \right)^2}$$

Then by partial fractions, and using Peirce formulas 298, 308 to integrate, we obtain upon simplification:

$$\int_0^{\frac{\pi}{2}} \frac{d\theta}{(K^2 \cos^2 \theta + 1)^2} = \frac{K^2}{2(K^2 + 1)^{3/2}} \left[\tan^{-1}(K + \sqrt{K^2 + 1}) - \tan^{-1}(K - \sqrt{K^2 + 1}) \right]$$

where the two arctan must be between $-\frac{\pi}{2}$ and $\frac{\pi}{2}$.

Now in terms of α , the half spray-angle, we have

$K = \tan \alpha$, $\sqrt{K^2 + 1} = \sec \alpha$, so equation (5) becomes

$$V_s' = \frac{4R^3 \tan^2 \alpha \cos \alpha}{3} \left\{ \pi + \sin^2 \alpha \left[\tan^{-1}(\tan \alpha + \sec \alpha) - \tan^{-1}(\tan \alpha - \sec \alpha) \right] \right\} \quad (6)$$

Let $\psi = \tan^{-1}(\tan \alpha + \sec \alpha)$

$\phi = \tan^{-1}(\tan \alpha - \sec \alpha)$

then $\psi - \phi = \tan^{-1} \tan(\psi - \phi)$

$$= \tan^{-1} \left[\frac{\tan \psi - \tan \phi}{1 + \tan \psi \tan \phi} \right]$$

But $\tan \psi = \tan \alpha + \sec \alpha$

$\tan \phi = \tan \alpha - \sec \alpha$

so $\psi - \phi = \tan^{-1} \left[\frac{\tan \alpha + \sec \alpha - \tan \alpha + \sec \alpha}{1 + \tan^2 \alpha - \sec^2 \alpha} \right]$

Now $\tan^2 \alpha - \sec^2 \alpha = -1$

$$\therefore \psi - \phi = \tan^{-1} \left[\frac{2 \sec \alpha}{0} \right]$$

$$= \frac{\pi}{2}$$

So the final equation is

$$V_s' = \frac{4}{3} R^3 \tan^2 \alpha \cos \alpha \left(\pi + \frac{\pi}{2} \sin^2 \alpha \right)$$

$$= \frac{2\pi}{3} R^3 \tan^2 \alpha \cos \alpha \left(2 + \sin^2 \alpha \right) \quad (7)$$

A plot of $\frac{V_s'}{R^3}$ vs. α is shown on Figure 18.

Figure 18. Relationship between α and $V_{s'}/R^3$

IX. BIBLIOGRAPHY

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