A Fluidized Bed Kinetic Model for the Fluorination of Zircon

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ABSTRACT

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ABSTRACT

Several reaction kinetic models for the fluorination of plasma dissociated zircon (PDZ) with hydrogen fluoride (for the production of zirconia) were developed. These models were fitted to reaction kinetic data obtained from a lab scale fluidized bed unit and the model that best fits the data was determined. The best fit model was reaction as rate-limiting step, with a shrinking core of PDZ in a porous matrix of zirconia (ZrO_2).

This model was used to develop models for a multi-stage fluidized bed reactor. These models, combined with a hydrodynamic fluidized bed model, facilitated the determination of an optimum multi-stage fluidized bed reactor configuration for the fluorination of PDZ.

The calculated optimum configuration and dimensions were used for the design of a pilot plant scale (200 metric tons/year of zirconia product) fluidized bed reactor. This reactor was built at the Atomic Energy Corporation of SA as part of its metal oxides research programme (METOX). The pilot plant reactor represents a tenfold scale-up from the laboratory unit.

The pilot plant reactor performed at design specifications, proving the validity of the developed model. Results obtained on the pilot plant unit compared excellently with predicted results from the model.

It was shown that a combination cross-/countercurrent multi-stage fluidized bed reactor could yield significant improvement over the conventional countercurrent multi-stage fluidized bed reactor for certain reaction kinetic conditions. This illustrates that effort put into the development of a proper reaction kinetic model can yield benefits in terms of reactor size, product yield and conversion, and ultimately plant capital and operating expenditure.

Key words: zircon beneficiation, fluidized bed model, fluorination, reaction kinetic model, plasma dissociated zircon, hydrogen fluoride, zirconia.

SAMEVATTING

Verskeie reaksie-kinetiese modelle is ontwikkel vir die gas-vastestof reaksie tussen HF en plasma-gedissosieerde sirkoon (PDS). Hierdie modelle is gepas op eksperimentele data vanaf 'n laboratoriumskaal sweefbed, en die model wat die data die beste pas is bepaal. Hierdie model is reaksie as snelheidsbeperkende stap, met 'n krimpende kern van PDS in 'n poreuse matriks van sirkonia (ZrO_2).

Hierdie model is gebruik om modelle vir 'n multistadium sweefbed te ontwikkel. Hierdie modelle, tesame met 'n hidrodinamiese sweefbedmodel, het die bepaling van 'n optimum multistadium sweefbed vir die fluorering van PDS gefasiliteer.

Die berekende optimum konfigurasie is gebruik in die ontwerp van 'n loodsskaal (200 metrieke ton sirkonia/jaar) sweefbedreaktor. Hierdie reaktor is gebou by die Atoomenergiekorporasie van SA, as deel van sy metaaloksiede-navorsingsprogram (METOX). Die proefaanlegsweefbed verteenwoordig 'n tienvoudige opskalering vanaf laboratoriumskaal.

Die loodsaanleg sweefbed het resultate gelewer volgens ontwerpspesifikasies, wat die geldigheid van die model bevestig. Resultate verkry van die loodsaanleg vergelyk baie goed met die model se voorspellings.

Daar is ook aangetoon dat 'n kombinasie teenstroom/-dwarsstroom sweefbedkonfigurasie 'n groot verbetering oor die konvensionele teenstroom sweefbed kan lewer vir toepaslike reaksiekinetika.

Sleutelwoorde: sirkoonveredeling, sweefbedmodel, fluorering, reaksiekinetiese model, plasma gedissosieerde sirkoon, waterstoffluoried, sirkonia.

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NOTATION

SYMBOL	DEFINITION	UNITS
a	Specific surface area of PDZ	[m^2/kg]
A	Area	[m^2]
A_d	Cross-sectional area of fluidized bed	[m^2]
A_{ext}	External surface area of particles	[m^2]
A_f	Pre-exponential or frequency factor (*units correspond to units of rate constant)	[*]
Ar	Archimedes number	[]
A_{sc}	Total surface area of shrinking cores of PDZ in particles for given mass of solids	[m^2]
$A_{sc,p}$	Surface area of shrinking core of PDZ in single particle	[m^2]
b	Constant defined in Equation 2.28	[m^2/s]
c	Dimensionless constant defined in Equation 2.16	[]
C_A	Average concentration of PDZ	[kmol/m^3]
C_{Ao}	Average initial concentration of PDZ	[kmol/m^3]
C_B	Concentration of HF gas	[kmol/m^3]
C_{Bo}	Initial concentration of HF gas	[kmol/m^3]
C_{Bs}	Concentration of HF gas at external solids surface	[kmol/m^3]
D_A	Gas diffusivity	[m^2/s]
D_{AB}	Binary mass diffusion coefficient	[m^2/s]
D_e	Effective diffusivity	[m^2/s]
D*	Particle diameter at which mass transfer and reaction rate resistances are equal	[m]
d_p	Particle diameter	[m]
d_{pa}	Area equivalent average particle diameter	[m]
d_{pm}	Mass-equivalent average particle diameter	[m]
d_s	Sauter mean particle diameter	[m]
d_{sc}	Diameter of shrinking core of PDZ	[m]
d_{sco}	Initial diameter of shrinking core of PDZ = d_p	[m]
E	Activation energy	[J/kmol]
E(t)	Residence time distribution	[]
F(t)	Cumulative residence time distribution	[]
f(t)	Function of time as defined in Equation 2.52	[]
g	gravitational acceleration	[m/s^2]
g_i	Cross-sectional area of subsection of reactor over total cross-sectional area	[]
h	Bed height	[m]
h_m	Convection mass transfer coefficient	[m/s]
h_{mf}	Bed height at minimum fluidization velocity	[m]
i	Number of reactor stages	[]
j_m	Colburn j factor for mass transfer	[]
k	General rate constant	[m^3/kg.s]
k_{bc}	Coefficient of gas interchange between bubble and cloud wake regions	[s^{-1}]

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SYMBOL	DEFINITION	UNITS
k_{ce}	Coefficient of gas interchange cloud wake region and emulsion phase	[s^{-1}]
k_{ED}	Rate constant for external diffusion as rate-limiting step	[m^3/kg.s]
k_f	Overall rate constant	[m^3/kg.s]
k_{ID}	Rate constant for internal diffusion as rate-limiting step	[m^3/kg.s]
k_m	Mass transfer coefficient	[m/s]
k_r	Reaction rate constant for first order reaction	[s^{-1}]
k_s	Rate constant for surf. area as solids reaction driving force	[m/s]
k_{wp}	Rate constant for PDZ mass as solids reaction driving force	[m^3/s]
k_{ws}	Rate constant for solids mass as solids react. driving force	[m^3/s]
M_{Ai}	Molar flow rate of PDZ OUT OF reactor stage i	[kmol/s]
M_{Bi}	Molar flow rate of HF INTO reactor stage i	[kmol/s]
m_p	Mass of particle	[kg]
m_{PDZ}	Mass of PDZ in a particle	[kg]
m_{PDZo}	Initial mass of PDZ in a particle	[kg]
$M_r(X)$	Molar mass of species X	[kg/kmol]
N_A	Number of moles of PDZ in reactor	[kmol]
N_{Ao}	Number of moles of PDZ in reactor at start of reaction	[kmol]
N_p	Number of particles in batch reactor	[]
$n(t)$	Function of time as defined in Equation 2.52	[m^{-1}]
P	Absolute pressure	[kPa]
p	Constant as defined in Equation 2.54	[kmol/m^3]
ΔP_b	Pressure drop over particle bed	[Pa]
ΔP_d	Pressure drop over distributor	[Pa]
Q	Volumetric flowrate	[m^3/s]
q	Constant as defined in Equation 2.54	[]
r	Radial distance	[m]
R	Particle radius	[m]
R_g	Gas constant = 8314	[J/kmol.K]
r_A	Reaction rate of PDZ	[kmol/s]
r'_A	Reaction rate of PDZ per unit bed height	[kmol/m.s]
Re_D	Reynolds number	[]
Re_p	Particle Reynolds number	[]
$Re_{p,mf}$	Particle Reynolds number at minimum fluidization	[]
s	Constant used in model rate equations	[m]
Sc	Schmidt number (ν/D_{AB})	[]
Sh	Sherwood number ($h_m d_p/D_{AB}$)	[]
t	Time	[s]
$\bar{t}$	Average residence time	[s]
T	Temperature	[K]
u_o	Superficial gas velocity through fluidized bed	[m/s]
u_b	Absolute bubble velocity	[m/s]
u_{mf}	Superficial gas velocity at minimum fluidization	[m/s]
u_t	Terminal velocity of a falling particle	[m/s]
V_{bed}	Volume of bed of particles	[m^3]
V_{PDZ}	Volume of shrinking core of PDZ in a single particle	[m^3]
W	Solids mass (including undissociated zircon)	[kg]

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SYMBOL	DEFINITION	UNITS
W_o	Initial solids mass	[kg]
W_{PDZo}	Initial mass of PDZ	[kg]
X_A	Conversion of PDZ to DPDZ or $(C_{Ao} - C_A)/C_{Ao}$ (does NOT include undissociated zircon contained in feed solids)	[]
Y	Initial mass fraction of PDZ in solids	[]
y	Variable bed height measured from distribution plate	[m]
z_{B0}	Mole fraction of HF in gas feed	[]

Greek Symbols

δ	Gas volume change due to reaction (moles of gas product minus moles of gas feed over moles of gas feed)	[]
ε_B	Gas volume change coefficient	[]
ε_m	Porosity of fixed bed	[]
ε_{mf}	Porosity of bed at minimum fluidization	[]
ε_p	Particle porosity	[]
ϕ_n	Thiele modulus for n-th order reaction	[]
ϕ_s	Sphericity of a particle	[]
γ_b	Volume fraction of solids in bubbles	[]
γ_c	Volume fraction of solids in cloud wake region	[]
γ_e	Volume fraction of solids in emulsion phase	[]
γ_i	The molar flow rate of PDZ out of stage i over the initial molar flow rate of PDZ $[M_{Ai}/M_{A0}=(1-X_{Ai})]$	[]
η	Internal effectivity factor as defined in Equation 2.47	[]
φ	Dimensionless constant as defined in Equation 2.44	[]
λ	Dimensionless constant as defined in Equation 2.44	[]
μ	Fluid dynamic viscosity	[Pa.s]
ν	Fluid kinematic viscosity	[m^2/s]
π	pi, or 3.141529654…	[]
ρ_b	Bulk density of feed solids	[kg/m^3]
$\rho_{b,t}$	Bulk density of solids as function of time	[kg/m^3]
ρ_g	Gas density	[kg/m^3]
ρ_{PDZ}	Solids density of core of PDZ (NOT bulk density)	[kg/m^3]
$\rho_{PDZ,b}$	Bulk density of PDZ in particle volume as function of time	[kg/m^3]
ρ_s	Solids particle density (NOT bulk density)	[kg/m^3]
σ	Constriction factor – accounts for variation in cross-sectional area	[]
τ	Tortuosity = (actual distance/shortest distance) between two points	[]