APPENDICES

Appendix A: Sample derivation of model equations

This appendix shows the derivation of the equation for PDZ conversion as function of time for reaction as rate-limiting step, with solids mass as solids driving force, as referred to in Section 2.3.1.2.

For this model, the rate equation is given by (as derived in Section 2.2.2.1):

$$\begin{gathered} -r_A = k_{ws}(1-cX_A)C_B \\ \left[k_{ws} = kW_o\right] \end{gathered} \qquad \textbf{(Eq A1)}$$

Taking a mole balance for HF over a differential reactor volume (where y is bed height measured from the distribution plate):

IN - OUT + GENERATED= STORED

$$A_d u_o C_B(y) - A_d u_o C_B(y+dy) - 4k_{ws}(1-cX_A)C_B dy = 0 \qquad \textbf{(Eq A2)}$$

Rearranging and integrating (with conversion X_A constant over bed height) gives the HF concentration as function of bed height:

$$\begin{gathered} \int_{C_{B0}}^{C_B} \frac{dC_B}{C_B} = -\frac{4k_{ws}}{A_d u_0}(1-cX_A)\int_0^y dy \\ \ln\frac{C_B}{C_{B0}} = -\frac{4k_{ws}y}{A_d u_0}(1-cX_A) \\ C_B = C_{B0}e^{-\frac{4k_{ws}y}{A_d u_0}(1-cX_A)} \end{gathered} \qquad \textbf{(Eq A3)}$$

Average HF concentration over bed height is given by:

$$\begin{gathered} \overline{C_B} = \frac{1}{h}\int_0^h C_B dy \\ \overline{C_B} = \frac{C_{B0}}{h}\int_0^h e^{-\frac{4k_{ws}(1-cX_A)}{A_d u_0}y} dy \\ \overline{C_B} = \frac{C_{B0}A_d u_0}{4hk_{ws}(1-cX_A)}\left[1-e^{-\frac{4k_{ws}h}{A_d u_0}(1-cX_A)}\right] \end{gathered} \qquad \textbf{(Eq A4)}$$

Taking a mole balance for PDZ over the reactor volume:

IN - OUT + GENERATED= STORED

$$0 - 0 + r_A = \frac{dN_A}{dt}$$
$$\frac{dN_A}{dt} = -k_{ws}(1 - cX_A)\overline{C_B} \qquad \textbf{(Eq A5)}$$

The number of moles of PDZ (N_A) in the reactor can be defined as follows:

$$N_A = N_{Ao}(1 - X_A)$$
$$\therefore dN_A = -N_{Ao}dX_A \qquad \textbf{(Eq A6)}$$

Through combination of Equations A5 and A6 and substituting for average HF concentration from Equation A4:

$$\frac{dX_A}{dt} = \frac{k_{ws}}{N_{A0}}(1 - cX_A)\overline{C_B}$$
$$\frac{dX_A}{dt} = \frac{C_{B0}A_d u_0}{4hN_{A0}}\left[1 - e^{-\frac{4k_{ws}h}{A_d u_0}(1-cX_A)}\right] \qquad \textbf{(Eq A7)}$$

Rearranging and simplifying:

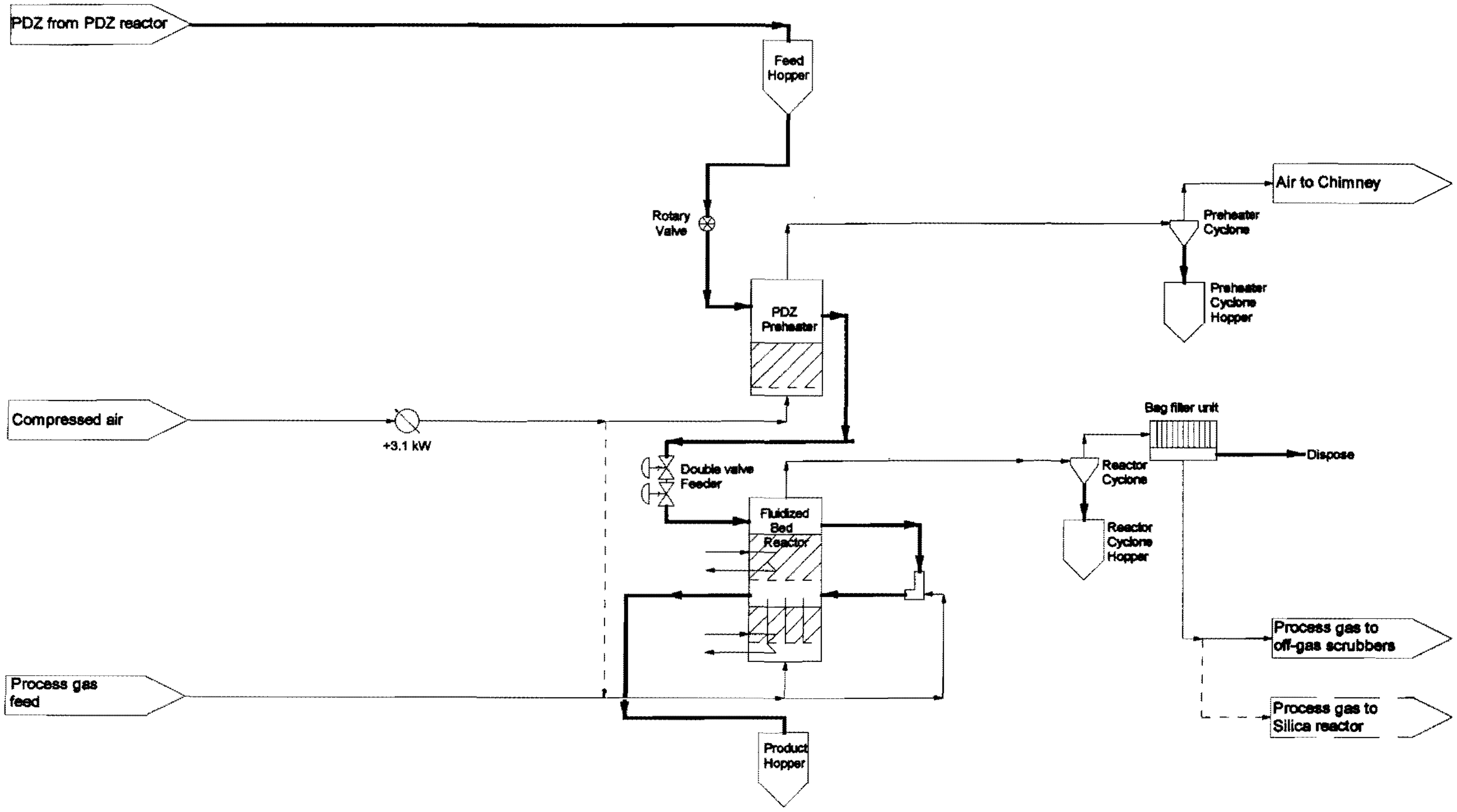
$$Set:$$
$$s = \frac{4k_{ws}h}{A_d u_0} \qquad \textbf{(Eq A8)}$$
$$\int_0^{X_A} \frac{dX_A}{[1 - e^{-s(1-cX_A)}]} = \frac{C_{B0}A_d u_0}{4hN_{A0}}\int_0^t dt$$

This last equation can be solved analytically using substitution and yields an implicit equation for PDZ conversion as function of time:

$$X_A - \frac{1}{sc}\ln\left[\frac{1 - e^{-s(1-cX_A)}}{1 - e^{-s}}\right] = \frac{C_{B0}A_d u_0}{4hN_{A0}}t$$
$$where \qquad \textbf{(Eq A9)}$$
$$s = \frac{4k_{ws}h}{A_d u_0}$$

Appendix B: Process flow diagram of pilot plant fluidized bed system

Process Flow Diagram: Phase 3 Fluidized Bed



Appendix C: Experimental conditions and results

Relevant experimental conditions, parameters used in reaction equations, and experimental and model results are presented here.

Gas physical properties were obtained from Perry[18], Chemical Engineering[29,30] and Janaf Thermochemical Tables[31].

Gas mixture properties (mixture density, viscosity, thermal conductivity and heat capacity) were calculated using mixing rules from Perry[18].

C1 Physical parameters used for PDZ bed material

Parameter	**Symbol**	**Value**	**Units**
Porosity of PDZ feed material	ε_m	0.453	[]
PDZ porosity at minimum fluidization	ε_{mf}	0.474	[]
Bulk density of PDZ	ρ_b	2200	[kg/m^3]
Particle density of PDZ	ρ_{PDZ}	3800	[kg/m^3]
Absolute bubble velocity*	u_b	0.209	[m/s]
Sauter mean diameter for PDZ	d_s	116	[µm]
Reaction gas volume change fraction	δ	-0.25	[]
Sphericity of PDZ	ϕ_s	0.6	[]

* Determined by video-recording bubble velocity in a one-dimensional perspex fluidized bed using PDZ as bed solids and nitrogen as fluidizing gas with a stopwatch and ruler positioned next to the bed.

C2 Laboratory operating conditions and batch reactor specifications for determination of the rate constant

Note: Laboratory fluidized bed reactor used a mixture of HF and nitrogen as feed gas.

Parameter	**Symbol**	**Value**	**Units**
Initial reactor bed load	W_0	11	[kg]
Conversion of feed PDZ	Y	0.91	[]
HF feed rate	C_{B0}	40	[mol/hr]
Reactor cross-sectional area	A_d	0.01	[m^2]
Volumetric flow rate of nitrogen	Q	1.5	[m^3/hr]
Nitrogen feed temperature	T_n	25	[°C]
Nitrogen feed pressure	P_n	20	[kPag]
Temperature of HF/N_2 mixture before reactor	T_m	100	[°C]
Gas mixture pressure before reactor	P_m	35	[kPag]
Pressure drop over reactor	ΔP	4.8	[kPa]

C3 Reactor conditions for modelling of different reactor configurations

Parameter	**Symbol**	**Value**	**Units**
Bed load: main stage A	W_A	100	[kg]
Bed load: main stage B	W_B	100	[kg]
Solids feed rate	M_{Ao}	0.245	[kmol/hr]
Conversion of feed zircon to PDZ	Y	0.90	[]
Feed concentration (HF)	C_{Bo}	8	[mol/m^3]
Superficial gas velocity	u_o	12	[cm/s]
Reactor cross-sectional area	A_d	0.22	[m^2]
Fraction of HF in feed gas	z_{B0}	0.5	[]
Reaction temperature	T_r	120	[°C]
Rate constant	k_s	5.89E-6	[m/s]

C4 Pilot plant reactor conditions for comparison of model to pilot plant experimental results

Parameter	**Symbol**	**Value**	**Units**
Bed load: main stage A	W_A	120	[kg]
Bed load: main stage B	W_B	120	[kg]
Solids feed rate	M_{Ao}	0.191	[kmol/hr]
Conversion of feed zircon to PDZ	Y	0.85	[]
Feed concentration (HF)	C_{Bo}	8	[mol/m^3]
Superficial gas velocity	u_o	9.5	[cm/s]
Reactor cross-sectional area	A_d	0.314	[m^2]
Fraction of HF in feed gas	z_{B0}	0.5	[]
HF feed flow rate	M_{B1}	0.94	[kmol/hr]
Gas inlet temperature	T_g	120	[°C]
Solids inlet temperature	T_s	120	[°C]
Gas mixture pressure before reactor*	P_g	-5	[kPag]
Rate constant	k_s	5.89E-6	[m/s]

* Pilot plant reactor was run under slight negative pressure

C5 Comparison of conversion between different reactor configurations as function of bed load (see Section 4.2.2.1)

Total bed load [kg]	**Conversion (3 st, CC) [%]**	**Conversion (5 st, CRC) [%]**	**Conversion (6 st, CRC) [%]**
60	38.9	73.7	81.2
120	55.5	91.0	95.9
140	59.2	94.7	98.2
160	62.3	97.2	98.9
180	64.9	98.4	99.5
200	67.2	99.2	99.8
240	70.9	99.4	99.9

C6 Comparison of different bed load distributions for equal total bed load (see Section 4.2.2.1)

Bed load distribution	**1:1:1:1**	**3:2:1:1**	**4:3:2:1**
Stage number	**Conversion [%]**	**Conversion [%]**	**Conversion [%]**
1	28	27	27
2	57	64	65
3	80	85	88
4	94	96	98
5	99	99.4	99.9
HF efficiency [%]	91.9	92.2	92.6

C7 Comparison of no gas mixing model to total gas mixing model

Stage nr.	**No gas mixing Conversion [%]**	**Total gas mixing Conversion [%]**
1	5.2	
2	12.4	
3	18.9	
4	23.6	27.0
5	57.0	63.0
6	81.1	84.9
7	94.2	95.8
8	99.1	99.4

C8 Comparison of steady-state conversion profiles between model and pilot plant reactor

Stage nr.	**Pilot plant Conversion [%]**	**Model Conversion [%]**
1	28.6	27
2	80.8	63
3	85.5	84.9
4	93.8	95.8
5	98.7	99.4

C9 Comparison of batch conversion profiles between model and pilot plant reactor

Time [hr]	**Pilot plant Conversion [%]**	**Model Conversion [%]**
0	0	0
0.5	13.3	
1.0	46.9	38.5
1.5	59.6	
2.0	76.9	76
2.5	88.8	
3.0	97.5	99.5
3.5	98.0	
4.0	100	100

WORD DEFINITIONS

Word(s)	***Definition***
Feed solids	The feed to the fluidized bed system or the product of the plasma dissociation system, consisting mainly of PDZ and some undissociated zircon. This is the general definition, except where specifically stated otherwise in the text.
Product solids	The product of the fluidized bed system, consisting mainly of DPDZ and containing some undissociated zircon and PDZ left over because of incomplete conversion. This is the general definition, except where specifically stated otherwise in the text.
PDZ	Plasma Dissociated Zircon - zirconia crystallites in an amorphous structure of silica.
DPDZ	Desilicated Plasma Dissociated Zircon - porous composite structure of zirconia crystallites.
CSTR	Continuously Stirred Tank Reactor – basic reactor model, with complete mixing and thus uniformly distributed conversion.
PFR	Plug Flow Reactor – basic reactor model, with uniform radial conversion and increasing conversion in the axial direction.
TDH	Transport Disengagement Height – height above the dense bed zone in a fluidized bed needed for disengagement of particles from off-gas.
CC	A multi-stage countercurrent fluidized bed reactor.
CRC	A combination cross-/countercurrent fluidized bed reactor with two main countercurrent stages and the second (or bottom) countercurrent stage divided into a number of crosscurrent stages.
ST	Total number of stages in fluidized bed reactor.

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