Simulation of titanium dioxide (TiO_2) ore elutriation from chlorination fluidized bed reactors

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Synopsis

Elutriation of solid reactants from fluidized bed reactors can affect their process performance and efficiency greatly. Chlorination fluidized bed reactors for selective conversion of solid metal oxides to metal chlorides are used widely these days. This study provides a platform for a proper understanding of reactant solid characteristics and solid shrinkage interaction with elutriation rate constants using multi-sized particles, sand-like, 'Geldart B' chloridable materials. The study has found that actual elutriation rates of the reactive system are influenced by complex parameters' interaction including bed diameter, reactor freeboard height, bed minimum fluidization velocity, and reactant's physical properties.

Introduction

Fluidization is known to be the effective applied method in different industries for solid particles' transformation into a fluid-like state, providing easy conveying and handling with rapid mixing of large amounts of solids. This has brought a continuous interest in developing fluidization processes in chemical and mining engineering, considering key design and scale-up parameters such as: reaction kinetics, flow hydrodynamics, and solid characteristics.

In 1944, the non-catalytic fluidized beds were acquired in industries other than petroleum for sulphide ore roasting, and one of the first units was constructed in 1947 for gold production by cyanidation. Since then these roasters progressively replaced existing technology centreing on multihearth roasters and rotary kilns, both in the sulphuric acid industry and for the preparation of a wide variety of solid materials needed in metallurgical industries[1]. The chlorination fluidized bed reactor was started in 1950 where rich titanium dioxide sand-like material is reacted with chlorine gas in a reducing atmosphere to produce titanium tetrachloride ($TiCl_4$). The titanium dioxide reacts exothermally as follows[2–5]:

$$TiO_2 + 2Cl_2 + C \rightarrow TiCl_4 + CO_2 \qquad [1]$$

This study focuses on titanium ore elutriation assessment at high temperature (800–1200°C) using different size and configuration fluidized beds to produce titanium tetrachloride ($TiCl_4$) widely used today for the synthesis of titanium metals, alloys, and pigments. With the main product of titanium chlorides, other metal oxides are chlorinated as well and produced. Two or more different feed ores are typically used for the fluidized bed chlorination process (e.g. rutile, anatase, and ilmenite). These two or more feed stocks have different structures, composition, and properties of titanium and metal oxides; however, two of these ores typically in use these days depend on raw material availability, plant design capability, and waste from metal chlorides with a method disposing of them. The typical chlorination fluidized beds are changed to suit different plant design capacities and engineering concepts. The loss of chlorine gas units in the waste streams are economically evaluated by the producing plants[6].

Few workers have attempted to simulate the performance of fluidized bed chlorinators; however, results were obtained in lab-scale reactors and assumptions were imposed to match model predictions with experimental data[7,8]. Specifically, solid elutriation from chlorination reactors can be significantly different at selected conditions in which elutriation rate estimation is not available based on the solid reactants' shrinkage behaviour.

A number of models have been developed and validated using experimental set-ups under carefully selected conditions for proper control of solid reactants' fine grain size, superficial gas velocity, reductant partial pressure, and different freeboard heights. Not considering other important factors such as; reactor size, configuration, design aspects, feed specifications, and bed composition, have

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 This paper was first published in the Industrial Fluidization South Africa, Conference (IFSA 2008), proceedings book, 19–20 Nov. 2008.

caused controversial findings in other studies[5,8] specifically on the effect of wider particle size distribution in other studies.

Ore elutration mathematical models

Titanium dioxide (TiO_2) ore elutriation analysis using an interactive chlorination model is developed, where typical operation and design scenarios are evaluated considering the interaction effect of gas and solids. The estimation and verification of reaction rates and elutriation constants for the purpose of general model development is conducted as well.

Sub-models for solids and gases (chlorine, carbon dioxide, carbon monoxide, and titanium tetrachloride) were used to study parameters' variation effect, a useful tool for basic understanding of different models' complexity and their limitations. An interactive model has combined the three different models (solid, gas, and elutriation) with the modified energy balance and has reflected the required interaction complexity of the system.

The solid model follows the shrinkage expression when particles of wide size distribution $P_0(r_i)$ are fed continuously with a rate of F_0 into a bed. At steady state condition (the weight of the bed is expressed as W), particles in the feed shrink continuously due to the reaction with gas and form a different particle size distribution in the bed $P_b(r_i)$ which is between the feed size and elutriation (entrained and carry over) size. The fine particles are elutriated and carried-over with the gas stream leaving the fluidized bed with a flow rate of F_2 and particle distribution of $F_2(r_i)$. The feed flow rate is shown as:

$$F_0(r_i) = F_0 P_0(r_i) \qquad [2]$$

The shrinkage model equation is derived from a material balance of the fluidized bed reactor considering solid feed, shrinkage reaction rate in the bed and the elutriation rate[1]. The wide particle size distribution of the solid reactant is used to generate size intervals (r_i), where shrinkage of solids occur causing a change in the particle size distribution in the bed and in the elutriation stream. In the following shrinkage model equation, the weight of each particle size interval in the bed is estimated as follows:

$$W(r_i) = \frac{F_0(r_i) - W(r_{i+1}) * \dfrac{Rate}{\Delta r_i}}{k(r_i) - \dfrac{Rate}{\Delta r_i} - 3 * \dfrac{Rate}{r_i}} \qquad [3]$$

The weight fraction of each interval is shown as:

$$P_b(r_i) = \frac{W(r_i)}{W} \qquad [4]$$

The total bed weight and the composition of the elutriated stream are:

$$W = \sum W(r_i) \qquad [5]$$

$$F_2(r_i) = W(r_i)k(r_i) \qquad [6]$$

$$P_2(r_i) = \frac{F_2(r_i)}{F_2} \qquad [7]$$

A number of parameters is included in the gas model, namely ore chlorination and coke combustion rates, gas concentration in both bubble and emulsion phases, and rate of gas consumptions. The elutriation rate constant and free board voidage models are:

$$kri = \rho_s U_{ts}(1-\varepsilon_i) \qquad [8]$$

$$\varepsilon_i = \left\{1 + \frac{\lambda(U_0 - U_{mf})^2}{2gD}\right\}^{-\alpha} \qquad [9]$$

Equation [10] is used to calculate λ:

$$\frac{\lambda \rho_s}{d_p^2}\left(\frac{\mu}{\rho_g}\right)^{2.5} = 12.3\mathrm{Rep}^{-2.5} D \qquad [10]$$

Equations [11]–[13] are for the drag coefficient (CD), particle Reynolds number (Rep) and solid particle velocity (U_{ts})[9]:

$$CD = \frac{10}{\sqrt{\mathrm{Rep}}} \qquad [11]$$

$$\mathrm{Rep} = \frac{d_p U_{ts} \rho_g}{\mu} \qquad [12]$$

$$U_{ts} = \sqrt{\frac{4gd_p(\rho_s - \rho_g)}{3\rho_g CD}} \qquad [13]$$

Note that, instead of using α values in different particle size intervals suggested by other studies[9] in Equation [10], α values are estimated based on typical operations of selected fluidized bed systems, which provide a more reliable result.

Results and discussion

Results have demonstrated that simple models, such as the solid shrinkage model for ore and coke, provide a useful understanding of the solid reactant behaviour and the parameters that influence bed performance. As well, it reveals the limitations of the solid models in understanding the complete behaviour, as the gas model is not included and certain assumptions are made.

Selected parameters were varied in the ore model and these parameters are expressed in definitions and terms that are useful for the interaction with the gas model. For example, a higher or lower elutriation rate of solid from the bed takes place for expected different gas velocities. The other design parameter is expressed here as reactor diameter (function of bed weight and bed height).

Reactor diameter variation

The number of parameters was varied and the effect on the reaction rate was demonstrated. The increase of bed diameter (or reactive bed weight) changed the reaction rate in the bed. Subsequently, it was then necessary to reduce the reactor temperature to reduce activity or maintain it at the same level with control on the elutriated (carried over or entrained) material.

Figure 1 shows that increasing bed diameter, and thus reactive bed weight, has not resulted in any appreciable change of the bed PSD. This conclusion was reached as well by other studies[10] using an experimental quartz reactor of 2.5 cm in diameter and 95 cm in length. This experimental lab-scale reactor had an expansion zone at the upper part to reduce the carry over (elutriation) of reactant particles. So, researchers appear in agreement on this finding, even when using different scale chlorinator bed reactors. Figure 2 shows that with increasing bed weight, the elutriation constants show a reverse effect, i.e. increasing bed weight reduces the elutriation constant, which is expected as per the model equation. Thus, with a higher bed weight, the thermal and hydrodynamic conditions of the bed (e.g. temperature, reactive gas concentration, and required superficial gas velocity) are know to achieve these elutriations constants as shown in other reported results. It is noticeable that increasing or reducing the elutriation constant values does not reduce or increase the absolute elutriation rates, as these rate constants represent a ratio of a specific particle size interval in the bed and in the elutriation stream.

To define the possibility of achieving the required hydrodynamics for the proposed higher weight condition, and subsequently the relevant elutriation constants, interaction of the solid and gas models is recommended and will be published in another paper.

Feed rate variation

Feed rate increase can result in a higher production of titanium tetrachloride. The increased production rate shows a linear increase of the reaction rate of solids (Figure 3). It is apparent that, due to the feed rate parameter variation while maintaining the elutriation rate as a controlled portion of ore feed and bed weight, the reactor is required to run at higher levels of reaction rates, thus thermally higher reaction temperatures are required, yet other kinetic modifications can be carried out to achieve the higher reaction rate. Note that higher temperature operations will lead to a higher consumption of coke and an undesirable CO/CO_2 gas products' ratio could appear.

For the economic viability of increased throughput, a fixed elutriation rate as a portion of the variable ore feed is controlled. Figure 4 shows that, with a fixed bed weight, elutriation constants are increased due to the increase of ore feed and subsequently the relevant increase of elutriation quantities.

Elutriation rate control

Many published correlations determining the elutriation rate constant are found; however, they were limited to the experimental conditions employed by each of the investigators and the setups used[11,12,13,14,15,16,17,18,19]. Extrapolation trials of these correlations to different operating conditions often lead to very strange results, for example, using some of the developed correlations to different reactor diameter such as higher excess gas flow, etc. A more reliable model was proposed and modified[11].

Consideration of elutriation rate constant control is given to bed diameter and height as design parameters as well as hydrodynamic conditions (minimum fluidization velocity, superficial gas velocity, gas density, gas viscosity) and selection of raw materials properties such as solid particle density.

Entrainment experiments using vessel diameter ranges from 1.9 cm to 14.6 cm concluded that at diameters greater than 10 cm, the elutriation becomes constant and independent of vessel diameter[20]. Other experiments of large-scale fluidized beds have reported that a sharp increase in elutriation is found compared to small-scale bed diameters, even at similar operating conditions[21]. This is explained as the significance of the wall effect will depend mainly on the fluidization regime at which the reactor is operating. For example, the column diameter effect diminishes if the friction of the particles is more important at high gas velocity[10].

Fluidized beds' scale-up presents attractive economics to chemical industries; however, elutriation control persists as a major concern for designers and operators equally. As the industrial developments continue the efforts to improve the knowledge of large-scale fluidized bed systems, thorough analysis of this issue is as important as the knowledge gained on the bed diameter effect. Large beds require certain precautions for a sustained performance specific to distributor plate design distributing gas sufficiently. Insufficient distribution area for the feed gas may cause an increase in the gas velocity in the bed and thus a sharp

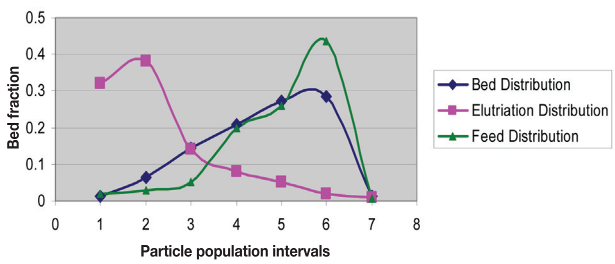

Figure 1—PSDs of bed, feed and carryover streams for different bed weight

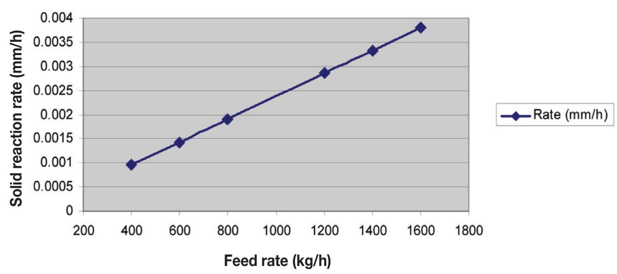

Figure 3—Reaction rate profile with changing feed rate

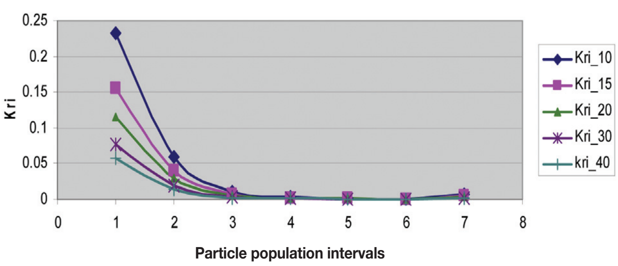

Figure 2—Elutriation constant profiles for different bed weights

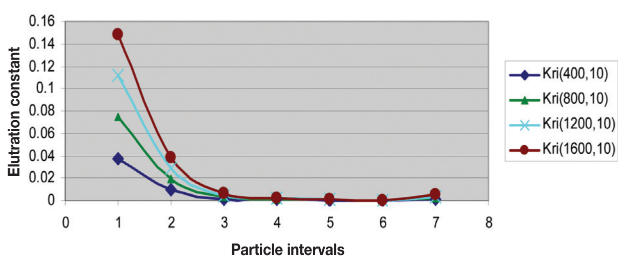

Figure 4—Elutriation rate constants profile

increase in the elutriation rate as well the proper selection and control of sustainable solid particle properties during the running mode of operation.

Figure 5 shows that, for the fluidization conditions under study, the diameter variation shows no effect on the elutriation rate constant values, which is in agreement with others' observations[10]. In general terms, large beds require careful attention to overcome the increased elutriation resulting from a higher throughput compared to smaller size beds. It is worth mentioning that the increase of the elutriation rate constant of interval 7 in Figure 5 is superficial, as this interval has added all particles coarser than the maximum size used, and thus the general trend of the elutriation rate constant reduction with higher particle intervals is maintained.

Bed hydrodynamics' variables, including the minimum fluidization velocity variation are believed not to have any effect on the elutriation rate[10]. Other researchers have reported that hydrodynamic variation may have caused a change in the elutriation rate constant[22]. Also, other bed hydrodynamics such as bubble size and bed internals may have contributed to the conclusion stated above. The distinction between elutriation rate and entrainment rate should be addressed carefully on different running systems with their own characteristics. Where, measurements of elutriation can be done below the total disengagement height (TDH) similar conclusion to others can be drawn[22]. The measurement above the TDH can still show a variation and the dependency of the elutriation rate on hydrodynamic properties.

Minimum fluidization velocity depends mainly on the number of parameters related to the solid and gas in the bed and not to the reactor and vessel geometry or volume. Specifically, it depends on particles, average diameter, solid density, gas density, and viscosity[9]. Therefore, the minimum fluidization velocity should not change when using the same system of solids and gases. So, both controversial conclusions about the dependency of the elutriation rate on bed hydrodynamics, namely minimum fluidization velocity, can be explained. In the case of operating processes where fluidized beds maintain the physical properties of the gas and solids, elutriation is not expected to be affected by bed hydrodynamics. However, for other beds, elutriation can be affected by the reduction or increase of the minimum fluidization velocity.

Operating fluidized beds encounter different elutriation rates when a change in bed properties results in a lower minimum fluidization velocity. Figure 6 shows that when fluidized beds have encountered a change in the minimum fluidization velocity, the elutriation rate responds to this change as well. For example, when a fluidized bed reduces its density with time due to the accumulation of low density impurities, the elutriation rate increases due to the shift of the bed minimum fluidization velocity to a lower level.

Effect of H/D ratio on scale-up

Larger reactor diameters represent different H/D ratios at different operating levels. The concept of maintaining the H/D ratio while bed volumes are scaled up is a common practice. For the same H/D ratio (0.75), moving from deep bed to shallow bed shows an increase in the elutriation rate (Figure 7). Also, two shallow bed cases have shown an increase of elutriation rates from the bed. The results obtained here agree with previous researchers' findings where there was a sharp increase in elutriation of a large-scale fluidized bed compared to small-scale bed diameters[21]. In other words, the increase in bed diameter while maintaining the gas flow conditions have increased elutriation rates. Note that the lowest H/D ratio of 0.70 has shown the highest elutriation rate from the reactor. This is due to the reduction of the bed operating level from 3.75 to 3.50 units while the diameter was maintained at 5.00 units. Meanwhile, the bed weight for this case has reached a higher value while volume is reduced. The high ore to coke ratio has resulted in this increase of weight, demonstrating the complex interaction of the system and the required control measures for system productivity.

The earlier analysis of the elutriation rate constant has concluded that the elutriation rate constants are insensitive to the reactor diameter variations. This conclusion agrees with other studies. However, the elutriation rate constants from the gas-elutriation-solid-interactive model are shown to be affected by reactor bed height as well as diameter, as shown in Figure 8. The shallow case of H/D=0.70 has shown a need to feed a reduced amount of nitrogen gas and increased feed of coke in order to maintain the preferable bed ratio of ore to coke.

Conclusion

The solid shrinkage model for ore and coke has provided a useful understanding of solid reactant behaviour and the parameters that influence chlorination fluidized bed performance.

Increasing or reducing elutriation constant values does not reduce or increase the absolute elutriation rates, as these rate constants represent a ratio of a specific particle size interval in the bed and in the elutriation stream.

Higher levels of reaction rates can yield higher throughput provided that higher reaction temperatures are acceptable. However, other kinetic modification can be carried out to achieve the higher reaction rate.

Minimum fluidization velocity change due to low density impurities' accumulation results in higher elutriation rates of the bed.

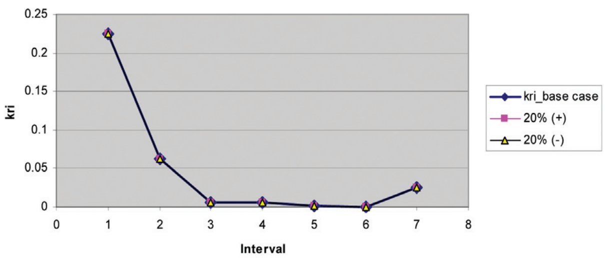

Figure 5—Effect of bed diameter on $k(r_i)$

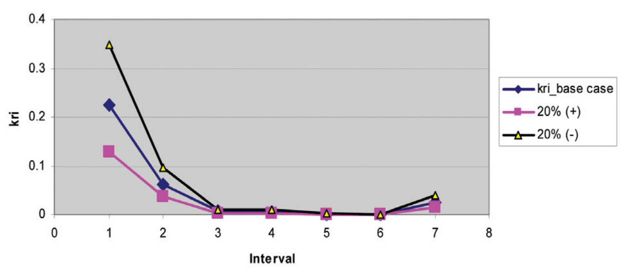

Figure 6—Effect of minimum fluidization velocity on $k(r_i)$

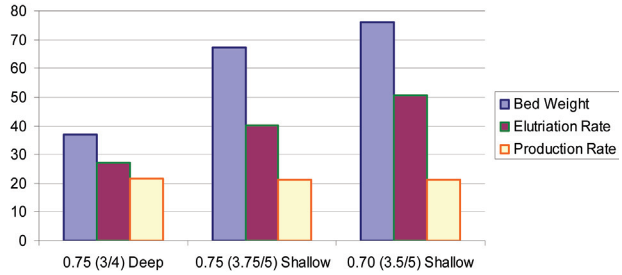

Figure 7—Elutriation rate of large volume shallow fluidized beds

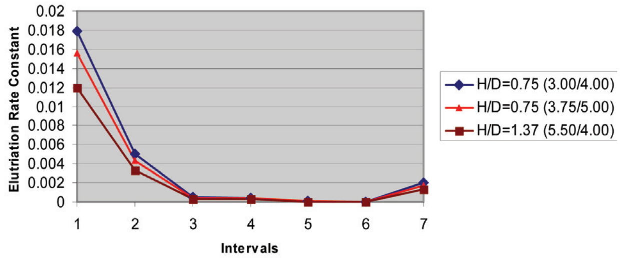

Figure 8—Elutriation rate constants of large volume shallow fluidized beds

Elutriation rate constants from the gas-elutriation-solid-interactive model are shown to be affected by reactor bed height as well as diameter.

Notation

d_P	Solid particle diameter
F_0	Feed rate of solid, kg s^{-1} (in equation 3.48, elsewhere in kg h^{-1})
$F_0(r_i)$	Flow rate of the solid feed stream per interval, kg h^{-1}
F_2	Elutriation rate of solid, kg s^{-1} (in equation 3.48, elsewhere in kg h^{-1})
$F_2(r_i)$	Flow rate of the elutriation stream per interval, kg h^{-1}
g	Gravitational constant
$k(r_i)$	Elutriation constant for the interval being evaluated, h^{-1}
kri	Elutriation rate constant, kg m^{-2} s^{-1}
$P_0(r_i)$	Weight fraction of each particle size interval in the feed stream
$P_2(r_i)$	Weight fraction of each particle size interval in the elutriation stream
$P_b(r_i)$	Weight fraction of each particle size interval in the bed
Rate	Rate constant for the shrinkage reaction, mm h^{-1}
r_i	Mean particle radius for the interval being evaluated, mm
U_0	Superficial gas velocity, m s^{-1}
U_{mf}	Minimum fluidization velocity, m s^{-1}
U_{ts}	Solid terminal velocity, m s^{-1}
W	Total solid bed weight, kg
$W(r_i)$	Weight of each particle size interval in the bed, kg
$W(r_{i+1})$	Weight of the next interval, kg

Greek letters:

Δr_i	Step size of the interval, mm
α	An exponent that depends on a particular particle size interval
ε_i	Freeboard voidage
μ	Gas viscosity (calculated as a function of bed temperature), cP
ρ_g	Gas density (calculated as a function of bed temperature), kg m^{-3}
ρ_s	Solid particle density, kg m^{-3}

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