Study of the agglomeration of alumina powders using in situ turbidimetry

Hubert Saint Raymond, Frédéric Gruy, Michel Cournil

STUDY OF THE AGGLOMERATION OF ALUMINA POWDERS USING IN SITU TURBIDIMETRY

SAINT-RAYMOND H., GRUY F. and COURNIL M.
Département SPIN, Ecole des Mines de Saint-Etienne
158 cours Fauriel- 42023 SAINT-ETIENNE CEDEX (France)

ABSTRACT

Kinetics of agglomeration of alumina powders in stirred aqueous solutions was studied by means of an in situ turbidity sensor. The effects of stirring rate, pH and concentration of additives were determined and analysed via a new model of brownian and turbulent agglomeration in presence of interactions.

Suspensions of solid powders in liquid media are used in many industrial processes, particularly in ceramics production. In most cases, it is of major interest to follow as continuously as possible the dispersion state of the suspension for practical reasons of control or characterisation, as well as for fundamental aims of interpretation or modelling.

Turbidimetry is one of the few techniques compatible with the use of in situ sensors; in recent studies (1, 2), we proved that it can be used to obtain continuous information on the particle size distribution in solid-liquid media in which attrition or agglomeration take place. The possibility of in situ measurements is essential in agglomeration studies, because sampling may alter the hydrodynamic conditions and damage the agglomerates.

In this paper, we present an experimental study of agglomeration of an alumina powder for ceramics materials. To this aim, we have designed a reactor equipped with a turbidimetric sensor. The effects of stirring rate, pH and additive concentrations on the dynamics of agglomeration are qualitatively and quantitatively determined. These experimental results are then discussed with the help of a model. This model consists of three parts:
i) determination of agglomeration kernels in brownian and turbulent conditions;
ii) solution of the population balance equation, taking into account agglomeration and setling ;
iii) calculation of the turbidity of the suspension.
This model has been written, assuming compact agglomerates; the consequence of a possible fractal structure is then examined.

EXPERIMENTAL SECTION

TURBIDIMETRY

Scattering of an incident parallel light beam by a particle results in a global extinction phenomenon in the forward direction. Mie has proposed a general solution to the extinction problem of a plane monochromatic wave by a spherical isotropic homogeneous particle in a transparent non absorbing medium (3). For a suspension of particles, the extinction phenomenon is described by:

$$\tau = \frac{1}{L} \ln\left(\frac{I_0}{I}\right) \qquad (1)$$

τ is defined as the turbidity of the system, I_0 is the intensity of the incident beam, I the intensity of the transmitted beam after an optical path of length L.

For a polydisperse population of N particles per unit volume characterised by the normalised distribution by number f (D) of the particle diameter D, turbidity is given by the following integral:

$$\tau = \frac{N\pi}{4} \int_0^{\infty} Q_{ext} D^2 f(D) dD \qquad (2)$$

If the values of the extinction coefficient Q_{ext} are available, integral (2) can be calculated using a discretisation in diameter. This determination is rather complicated and requires the knowledge of the refraction indices of the different media (3). Conversely, the PSD of a suspension can be obtained from its turbidity spectrum using optimisation (4) or inversion (5) algorithms. This type of determination has been done successfully in recent studies (1, 6, 7). However, in the case of an agglomerating suspension, the problem is made difficult by the rapid broadening of the distribution and the results obtained are not reliable enough. For this reason, the validity of the models will be judged, from the comparison between variations with time of predicted and observed turbidity.

MATERIALS AND REACTOR

Agglomeration has been studied on an alpha alumina powder for ceramics. Its initial PSD, obtained from laser particle sizing (Coulter LS 130) shows two main peaks around 0.3 µm and 2 µm with respective proportions of 15% and 85% by weight (99% and 1% by number). Alumina zeta potential (ζ) has been determined at different pH values (laser Zee Meter, Pen Kenn equipment). The zero point of charge is observed at pH = 9.

The agglomeration experiments have been carried out in a vessel of capacity 0.5 l, equipped with three baffles and a four-blade 45° impeller. A ultrasonics probe can be used to homogenise the suspension and to break the agglomerates. The turbidity sensor is fixed at the bottom part of the vessel (Fig. 1). A polychromatic light beam is led to the measurement cell by optical fibres. After crossing the sensor window, where it is scattered by the particles in suspension, the transmitted light is led again via optical fibres to 32 photodiode array spectrophotometer which delivers the turbidity spectrum of the suspension (8). The hydrodynamics of the reactor, in particular its turbulent state, has been characterised by Doppler Laser Anemometry (DLA).

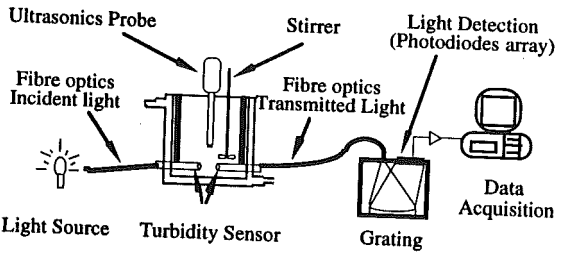

Fig 1 Experimental set-up

Agglomeration was studied in water at different pH values obtained by hydrochloric acid or sodium hydroxide additions ; in some experiments, ammonium citrate and ammonium polyacrylate, known as dispersants in ceramics powder processing, have been added. Turbidity is recorded during the different stages of each experiment (Fig. 2). Turbidimetry requires very low values of volume fraction in solid ($< 10^{-4}$).

EXPERIMENTAL RESULTS

- Influence of pH (Fig. 3): a strong influence is observed ; the suspensions of alumina in water are nearly stable at pH = 4, whereas they rapidly agglomerate at pH = 9.5.

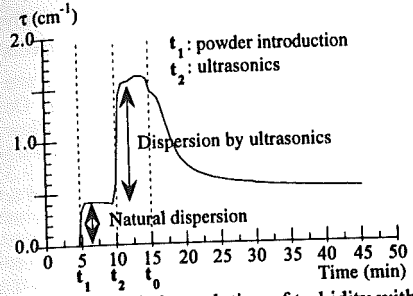

Fig 2 Characteristic evolution of turbidity with time during an agglomeration experiment

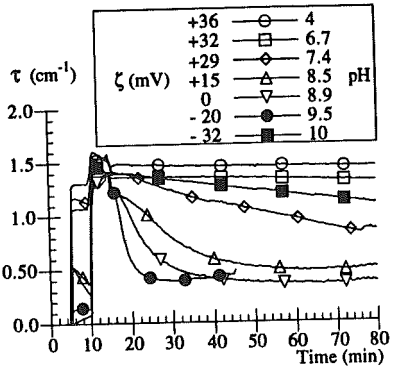

Fig 3 Influence of pH on alumina agglomeration in water at 350 rpm

- Influence of the stirring rate (Fig. 4): even in favourable conditions (pH = 8.5) and without agitation, agglomeration occurs very slowly. The agitation considerably accelerates the phenomenon.

- Influence of dispersants: ammonium citrate slightly reduces agglomeration with a maximum effect at a concentration of 0.09 weight %. Ammonium polyacrylate strongly reduces agglomeration, in particular in the range of 0.2 - 0.3 weight % (Fig. 5).

- Other experiments (8) have proved the reversibility of agglomeration after ultrasonics breakage of the agglomerates.

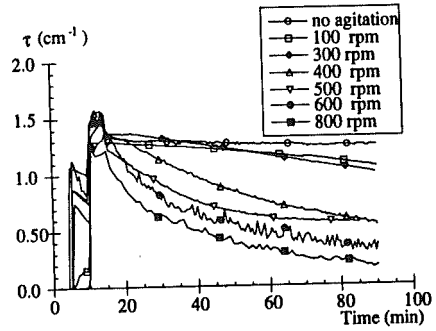

Fig 4 Influence of stirring rate on alumina agglomeration in water at pH 8.5

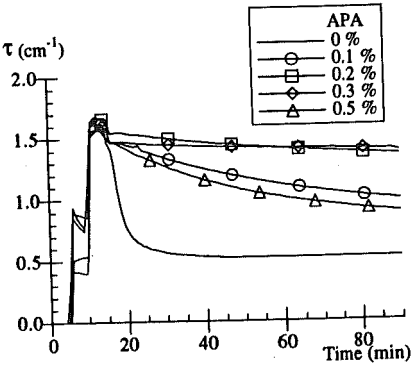

Fig 5 Influence of ammonium polyacrylate (APA) on alumina agglomeration in water at 350 rpm

- Sedimentation -which was observed in some experiments- has been quantitatively studied, using the same experimental set-up (8) with aluminas of several diameters.

DISCUSSION

QUALITATIVE DISCUSSION

The continuous decrease in turbidity as agglomeration proceeds can be essentially explained by the decrease of particle number (Eq. 2). In acid (pH ≤ 6.7) or basic media (pH ≥ 10), agglomeration is very weak; in these two pH zones, the absolute value of zeta potential is greater than 30 mV, which corresponds to a strong repulsive interaction. On the contrary, in the 8.5 - 9.7 pH zone, the very low values of zeta potential allow agglomeration to occur. The effect of the stirring rate is to increase the number of collision between particles and/or agglomerates. The small effect of ammonium citrate at pH = 9.5 is confirmed by experiments on slurries of ceramics powders. In fact ammonium citrate is mostly used in acid media or to reinforce the effects of other dispersants such as ammonium polyacrylate. The effects of this latter observed in our experiments are quite consistent with results obtained for slurries (9) ; with our set-up, we are able to quantify them; they can be interpreted as electrosteric effects (8).
The representativeness of our experimental results for an application to the case of concentrated slurries is certainly questionable because of the very low solid volume fractions which were used in this work ; however these results have the interest to emphasize, to quantify or to model several fundamental aspects which are also present at higher concentration.

QUANTITATIVE MODEL

The validity of the agglomeration models will be judged from the quality of the agreement between observed and predicted τ (t). For the calculations of τ (t), integral (2) is used. The way to determine the extinction coefficients Q_{ext} has been explained in (1, 8). In Eq. (2), N and f (D), can be obtained from the solution of the population balance equation of the system (10). The discrete form of this equation is:

$$\frac{dN_i}{dt} = \frac{1}{2}\sum_{j=1}^{i-1} K_{j,i-j}\, N_j\, N_{i-j} - \sum_{1}^{\infty} K_{ik}\, N_i\, N_k - k_{sed}\,(D_i)\, N_i \qquad (3)$$

where: $N_i \equiv N\, f\,(D_i)$.

Diameter D has been discretised in 649 size classes of variable width, covering the range [0.2 µm - 20 µm]; $K_{i,j}$ denotes the agglomeration kernel of i-mers and j-mers; k_{sed} is a kinetic constant which describes the settling phenomenon. particles (8).

The sedimentation constant k_{sed} has been deduced from experiments results which are not reported here. We can express it in a form consistent with the theory of Molerus and Latzel (11), i.e.:

$$k_{sed}\,(D_i) = m_1\, D_i^2 - m_2\, D_i\, \omega \qquad (4)$$

m_1 and m_2 are constants and ω is the rotation rate of the stirrer.

The determination of the agglomeration kernels K_{ij} requires several steps:

i) estimation of the average energy dissipation rate per unit volume $\bar{\varepsilon}$; the experimental results obtained by DLA are consistent with the expression proposed by Baldi et al.. (12)

ii) determination of the critical particle diameter D_c for which brownian diffusion and turbulent diffusion are comparable. From Levich model (13), $D_c = 0.76$ µm for $\omega = 350$ rpm. This means that it is essential to consider brownian agglomeration. Using Adachi et al.(14) approach, we obtain :

$$K_{i,j} = 0.5(K_{i,j})_{brownian} + (K_{i,j})_{turbulent} \quad (5)$$

$$(K_{i,j})_{brownian} = \frac{2kT}{3\mu}(D_i + D_j)\left(\frac{1}{D_i} + \frac{1}{D_j}\right) \quad (6)$$

where k is the Boltzman constant, T the temperature, µ the viscosity.

iii) calculation of $(K_{i,j})_{turbulent}$. So far, there exists no complete model of calculation of the turbulent kernel. Higashitani et al. (15) consider the case of only attractive interactions between particles, whereas Van de Ven and Mason (16) take also into account repulsive interactions, however only for the case of identical particles. In a recent work (8), we suggested to adapt the approach of Levich (13) based on the concept of turbulent diffusion : we replaced the brownian diffusion coefficient by the turbulent diffusion coefficient in the purely brownian expression of the particle diffusion flux proposed at first by Fuchs (17), then modified by Spielman (18) to take into account the electrostatic and hydrodynamic interactions.

The last step is to express the total interaction potential as the sum of the double layer repulsive and the retarded Van der Waals attractive potentials (19, 20). With this approach, the main results of (15) and (16) are retrieved, and a complete calculation of $(K_{i,j})$ turbulent is possible in all cases. Solution of equations (3) and calculation of τ (t) from equation (2) have been implemented on a 75 MHz Pentium PC.

The simulation results are in agreement with the experimental results, as far as the effects of pH and stirring rate are concerned, however, only in the first stage of agglomeration. Afterwards, the observed process rate is considerably higher than the predicted value.

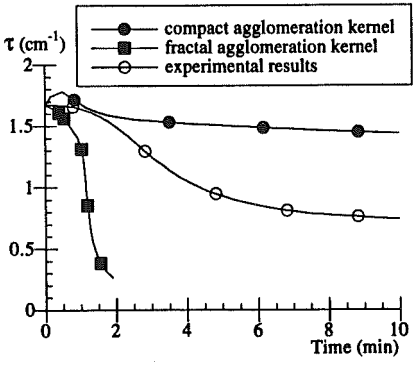

Fig 6 Comparison between experimental and calculated turbidity curves

Such an acceleration has been already mentioned by De Boer et al. (21) and Kusters (22). According to Kusters, this behaviour is due to the formation of ramified or even fractal agglomerates. To test this possibility, we assumed a fractal dimension of 1.89 for the agglomerates (ballistic model of (23)). Modifying the agglomeration kernel, we found a very rapid variation of turbidity with time (Fig. 6). The location of the experimental curve τ (t) is intermediate between the curves obtained for compact agglomerates and for fractal agglomerates. This position is consistent with the assumption of non compact agglomerates.

CONCLUSION

Turbidimetry has been used to characterise in situ the dynamics of agglomeration of alpha alumina in stirred aqueous media. The influence of pH, stirring rate and dispersants has been so quantitatively determined. A comprehensive model of agglomeration has been set-up; it confirms the observed effects of pH and stirring rate in the first instants of the process; however the experimental rate is higher than the predicted rate, probably due to the formation of non compact agglomerates. Due to the limitations of the measurement technique, the range of solid volume fraction investigated in this work is unrealistic, compared to the slurries concentration met in the ceramics production. However this study allowed us to emphasize several fundamental aspects which are also present at higher concentration.

LITERATURE CITED

1. Crawley, G.M., PhD thesis, INP Grenoble, France (1994).
2. Masy, J.C., M. Cournil and M. Lance, Chem. Res. and Technol. (1995) accepted.
3. Kerker, M., The scattering of light and other electromagnetic radiation, Acad. Press, New York (1969).
4. Melik, D.H. and H.S. Fogler, J. Coll. Inter. Sci., 92, 161 (1983).
5. Eliçabe, G.E. and L.H. Garcia Rubio, J. Coll. Inter. Sci., 129, 192 (1989).
6. Crawley, G.M., M. Cournil and D. Di Benedetto, Powder Technol. (1995) submitted.
7. Crawley G.M., F. Gruy and M. Cournil, Chem. Eng. Sci. (1995) submitted.
8. Saint-Raymond, H., Ph.D. thesis, INP Grenoble, France (1995).
9. Valdivieso, F., PhD thesis, Ecole des Mines, Paris (1995).
10. Randolph, A.D. and M.A. Larson, Theory of particulate processes, Acad. Press, New York (1988).
11. Molerus, O. and W. Latzel, Chem. Eng. Sci. 42, 1423 (1987).
12. Baldi, G., R. Conti and E. Alaria, , Chem. Eng. Sci. 33, 21 (1978).
13. Levich, V.G., Physicochemical hydrodynamics, Prentice Hall, New York (1962).
14. Adachi Y., M.A. Cohen Stuart and R. Fokkink, J. Coll. Inter. Sci., 165, 310 (1994).
15. Higashitani, K., K. Yamauchi , G. Hosokawa and Y. Matsuno, J. Chem. Eng. Japan, 16, 299 (1983).
16. Van de Ven, T.G. and S.G. Mason, Coll. and Polymer Sci., 255, 468 (1977).
17. Fuchs, N., Z. Physik, 89, 736 (1934).
18. Spielman, L.A., J. Coll. Inter. Sci., 33, 562 (1970).
19. Derjaguin, B.V. and L. Landau, Acta Phys. Chim. USSR, 14, 633 (1941).
20 Verwey, E.J.W. and J.T.G. Overbeek, Theory of the stability of lyophobic colloids, Elsevier, Amsterdam (1948).
21. De Boer, G.B.J., C. De Weerd and D. Thoenes, Chem. Eng. Res. Des., 67, 308 (1989).
22. Kusters, K.A., PhD thesis, TU Einhoven (1991).
23. Potanin, A.A., J. Coll. Inter. Sci.., 145, 140, (1991).