AGITATION EFFECTS IN PRECIPITATION

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Abstract

Though the main criteria for the selection of precipitator agitation system are suspension uniformity, engineering reliability and cost, recognition of how agitation affects the different crystallisation mechanisms should lead to improved selection and performance. These aspects of precipitator agitation are discussed. It is shown that both agglomeration and breakage of the hydrate particles are significantly affected by agitation. The extent of agglomeration decreases sharply with increased power input for agitation. High agitation rates also cause particle fracture. Attritive formation of small particles persists even at low agitation rates.

Introduction

Practical questions which come up during design and engineering of Bayer precipitation systems include:

a) Should operations be batch or continuous?

b) What should be the size and number of tanks to give the desired residence time?

c) What tank geometry- agitation system is to be provided?

These questions are important, though probably with some difference in emphasis, for European "floury" alumina as well as for American "sandy" alumina.

The present paper is concerned with the last question. The main expectations from the agitation system have been summarised in the paper "Agitation of decomposers" presented by Dr. Arnswald of VAW at an earlier AIME conference (1971). He and various other authors have pointed to the fact that Bayer precipitation is reaction rate controlled and is not dependent on diffusional processes. This means that the rate of hydrate precipitation remains practically unaffected by agitation as long as hydrate settling to the bottom of the tank is avoided and reasonably uniform suspension is maintained. The main criteria for agitator selection are then power consumption, engineering reliability and cost. Other practical considerations are the ability of the agitator to re-establish suspension after a certain shut-down period and possible role in reducing scale growth. In the present paper we focus attention on how agitation could affect precipitation in other ways and influence the product size distribution and indirectly the production rate. These effects could be important depending on the type of hydrate one wants to produce. Their recognition should lead to improvements in precipitator design and performance.

Published information on the role of agitation in precipitation is scant. These are mostly by European workers and the emphasis is on what effect agitation has on the precipitation rate, that is on the rate of formation of solid phase hydrate. Pearson (1955) in his well known monograph stated that "the rate of decomposition increases with stirring rate until the seed is completely dispersed.

D. Donaldson and B. E. Raahauge (Eds.), *Essential Readings in Light Metals*

It then remains virtully constant until the stirring becomes so vigourous that fresh particles are formed through attrition". Kanehara (1971) has recently shown how the precipitation rate constant remains practically unaffected with increasing agitator power input. Ivecovic and Jaserevic (1963) presented some results of agitation effects in the 1st ICSOBA conference. They showed that the precipitation rate was higher at the higher mixing speeds. A finer product was also obtained. Some Soviet publications (Tuyrin,1964) have reported that precipitation in an ultrasonic field causes the formation of small mono-crystals of the hydrate compared to the usual polycrystalline Bayer hydrate.

Crystallisation Mechanisms in Precipitation

A satisfactory description of Bayer precipitation is only possible by identifying the individual crystallisation mechanisms which operate during the formation of solid phase hydrate in seeded precipitation. The so called precipitation rate is a lumped effect which combines all these mechanisms. When analysing the role of agitation, which affects the different crystallisation mechanisms in different ways, a clear picture cannot be obtained by considering precipitation rate alone.

The different mechanisms known to be operating during precipitation are:

a) Nucleation: Birth of new crystals by molecular assembly.

b) Growth : Crystal size enlargement by molecular deposition.

c) Agglomeration: Physical size enlargement by particle assembly accompanied by a decrease in particle population.

d) Breakage including attrition: Size degradation accompanied by population accretion.

A realistic model of Bayer precipitation can be constructed by combining kinetic relations for these mechanisms with material, energy and population balances (Misra & White (1971)).

We then ask what effect has agitation on these individual mechanisms and how sensitive are the final product size distribution and production rate to such effects.

Effect of Agitation on the Different Crystallisation Mechanisms

a) Nucleation

Nucleation is the formation of new crystals (nuclei) of very small size within the solution. These can form spontaneously or due to the presence of seed crystals. The latter type is commonly known as "breeding" or "secondary" nucleation. Nucleation theory, as it stands at present, is inadequate to quantitatively describe this type of phenomena.

It has been found that in Bayer precipitation nucleation is best regarded as "breeding" type. It is significantly affected only by temperature and supersaturation and shows little sensitivity towards agitation. In seeded caustic aluminate solutions of usual Bayer process composition the nucleation rate decreases rapidly with increasing temperature and is negligible at 75 °C and above. Unfortunately, quantitative information on nucleation in Bayer precipitation is practically non-existent. Studies on other crystallisation systems (Clontz & McCabe (1971)) has shown that breeding nucleation is related to the frequency and energy of impact between seed crystals and between the crystals and equipment surface. Increased agitation should hence be expected give higher nucleation. This has not been found to be the case in Bayer precipitation. Control over nucleation is important in plants producing sandy alumina; here one usually operates with a temperature-supersaturation profile which minimises nucleation.

b) Growth

Convincing evidence is available that crystal growth during Bayer precipitation is controlled by the surface reaction mechanism and not by the diffusional step. This means that agitation will have little effect on crystal growth rate. Thus no significant improvement in growth rate will be achieved by employing agitator power inputs above that required to keep the coarser hydrate particles in suspension.

c) Agglomeration

It is generally recognised in the alumina industry that agglomeration of many small hydrate particles to form a larger particle can occur during precipitation. Agglomeration is desirable when producing a coarse alumina since it results in coarsening the product at the cost of unwanted fines. Evidence of agglomeration effects have been given by Scott (1963), Misra & White (1971) and Sakamoto et. al. (1971). It has been suggested that agglomeration can give rise to liquor inclusions which increase the soda content of the product.

By analogy with other flocculation processes, the following two step model has been proposed for agglomeration:

[Original individual particles in suspension] —Relative motion + Surface forces (Reversible)→ [Aggregate] →

—Cementation by crystal growth (Irreversible)→ [Agglomerate]

This model proposes that agglomeration occurs in two stages. Particle - particle encounters caused by relative motion are preserved by surface forces leading to the formation of flocs or aggregates. Progressive crystal growth cements the particles in the aggregates together to form agglomerates.

By providing relative motion, agitation assists aggregation. If sufficiently strong, agitation could also cause the aggregates to break up due to hydrodynamic forces. The steady state aggregate size is then the result of the dynamical balance between aggregation and break up. This description of the effect of agitation in flocculating systems has been duscussed by Thomas (1964) and others. Thus the extent of agglomeration should be strongly dependent on the degree of agitation. For the second part of the model, i.e. cementation, to succeed, sufficient supersaturation should be available to cause cementation of the hydrate particles by crystal growth.

The effect of agitation on agglomeration under Bayer process conditions was studied experimentally in small (1&5 liter capacity) laboratory crystallisers using synthetic Bayer liquor and technical seed hydrate. Particle size analyses were carried out by the Coulter counter.

It was found that the smaller (normally $< 20\ \mu m$) hydrate particles agglomerate under certain conditions. These agglomerates differed very little from the growing polycrystalline seed except for the markedly elongated forms of some of the agglomerates compared to the generally spherical appearance of the seed crystals. The occurance of agglomeration was, however, evident from the significant decrease in the small particle population. Photomicrographs of product from fine seed after advancing time periods are shown in Figure-1. These show the sequence of steps leading to the formation of agglomerates from several fine particles. The effect of agitator speed, on the agglomeration effect is shown in Figure-2 for a typical set of test results. At the highest power input rate tested (corresponding to an agitator speed of 1570 rpm), considerable particle breakage was observed which is evident from the particle size distribution data and photomicrographs shown in Figure-3. The relationship between estimated agglomerate size and agitator speed for the particular precipitator geometry/agitator combination is shown in Figure-4. The slope of the line was found to increase with increased seed quantity. These tests were carried out under negligible nucleation conditions. Results of many such tests showed that the extent of agglomeration is very sensitive to the degree of agitation.

In general "pachuka" air lift precipitators could be particularly unsuitable when a high degree of agglomeration is desired in order to produce a coarse hydrate. This is because the high shear rates in the two phase regimes of the central air pipe reduces the aggregate size. Slowly rotating, mechanical (e.g. paddles) agitators offer better opportunities for agglomeration.

d) Attrition and breakage

Degradation of particle size is to be expected when a solid - liquid suspension is agitated. If the agitation is vigourous, gross fracture of the particles could occur. This is avoided at lower agitation rates but attritive erosion of the particles could still be occuring. By attrition is meant the chipping off of small fragments from the particle surface after particle - particle or particle - vessel wall/agitator blade collision. This leaves the parent particle practically unchanged in size but generates a large number of fine particles. For example a 0,1 μm change in the size of a 70 μm hydrate particle would correspond to the formation of nearly 200 small particles of 2 μm size or about 1500 particles of 1 μm size. The net effect of attrition is thus to increase the small particle population without affecting the larger particles. If we assume that the small particles grow by the same amount as the larger particles (McCabe ΔL law) then the final size distribution (by weight) gets skewed towards the smaller size.

Attrition and breakage tests were carried out in the laboratory precipitators using just saturated synthetic caustic aluminate liquor and technical seed hydrate. In these tests gross breakage was observed at relatively high agitation levels. The appearance of broken fragments from 50 - 90 μm seed under progressively increasing agitator speeds is shown in Figure-5. The high rates of power input to cause gross fracture is normally not necessary in industrial precipitators. But calculations show that these rates could be approached in localised regions e.g. in the lift pipes of pachuka precipitators and in the annular space between the draft pipe and propeller in draft tube/propeller systems.

It was observed that attrition persisted even under considerably lower agitation rates than that needed to cause gross breakage. Photomicrographs in Figure-6 show the effect of attritive erosion on large seed hydrate (100 to 120 μm) which was slowly agitated (agitation sufficient only to avoid settling) in just saturated Bayer liquor for 8 hours. The irregular sharp edges have chipped off yielding rounded particles.

Figure-7 is an example of the change in small particle population when seed hydrate (50 g./lit., + 53-85 μm) was agitated at low power inputs. Under these conditions practically no changes occured in the population above about 5 μm size. Below this size, counts progressively increased with time. The smaller the size the faster was the population rise.

In the particular precipitator arrangement studied the rates of formation of the different sized attrited particles could be correlated by the relation:

$$\frac{dN(\ell)}{dt} = k\,(A - \ell)^{3.75}$$

where ℓ is the size of the attrited particle, $N(\ell)$ is the number of particles of size l per ml. of suspension and t is time in hours. A and k are constants depending in the agitator power input; numerical values for these at low power inputs are 5.1 and 2.5×10^3 respectively. The total rate of generation of new particles of all sizes (detectable) by attrition under low power conditions was approximately 10^6 particles per hour per ml. of suspension.

These results show that attrition is an important and sensitive source of fine particles during precipitation. This is particularly worth watching when a coarse sandy alumina is the desired product. In the case of floury alumina, nucleation is likely to predominate over attrition as the principal source of new particles.

Conclusions

Agitation affects the different crystallisation mechanisms involved in precipitation in different ways. A knowledge of these is important to tailor the agitation system which will yield the desired product size distribution and still maintain high product recovery. Observations carried out in model precipitators show that agglomeration, breakage and attrition of hydrate particles are strongly sensitive to the agitation characteristics. These factors deserve to be included in the criteria for agitator selection apart from such practical considerations as ability to maintain uniform suspension, power consumption and cost.

The main part of the work reported here was carried out in small laboratory precipitators. Qualitative supporting data have been obtained from limited industrial tests. We welcome information and comments relating to industrial experience in this area.

Acknowledgements

This study was carried out at the Department of Chemical

Engineering, University of Queensland, Australia and was supported by a Comalco Industries Research Fellowship. Helpful suggestions and comments by Dr. E.T. White are gratefully acknowledged.

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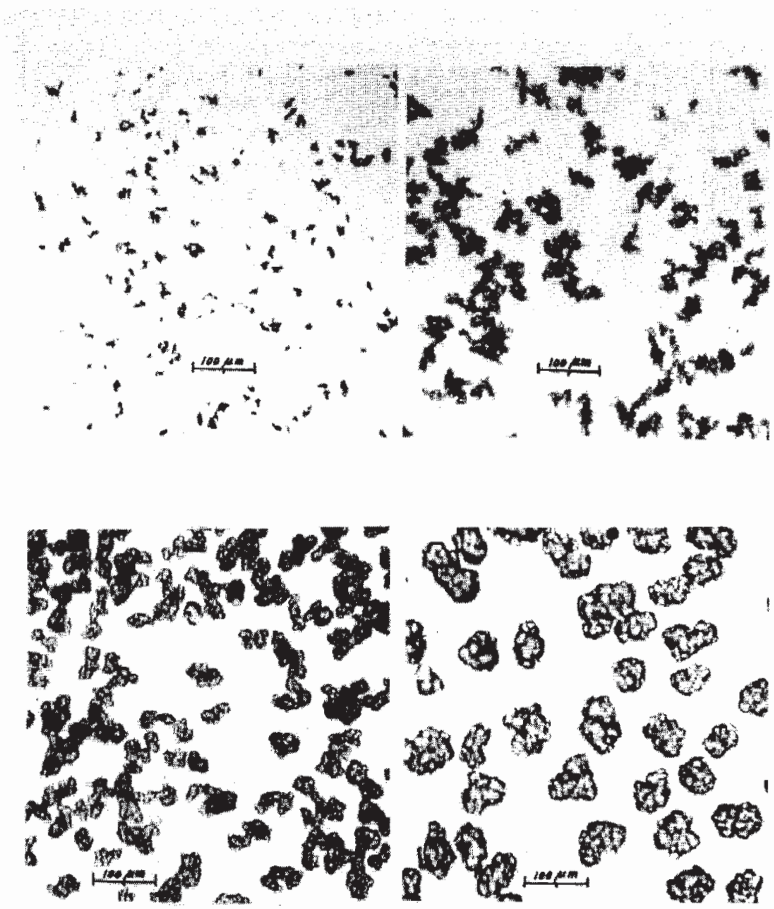

Fig.-1 Agglomeration & growth of small particles

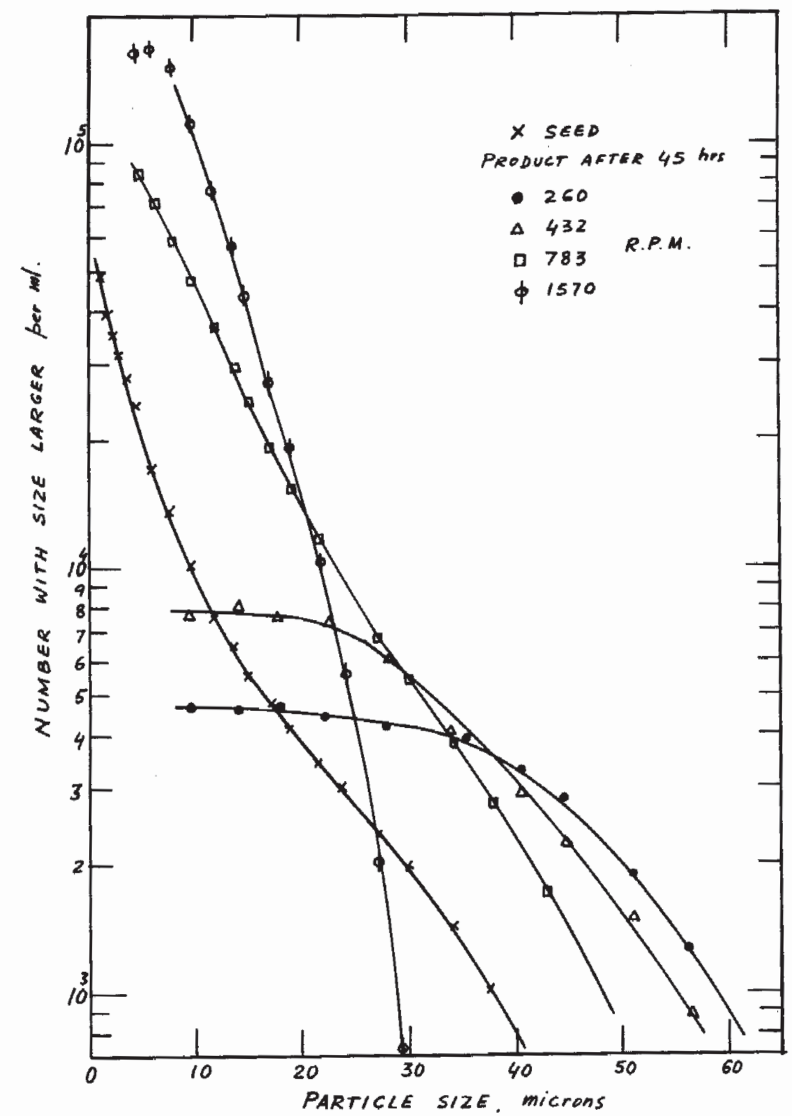

Fig.-2 Change in size distribution due to agglomeration and growth.

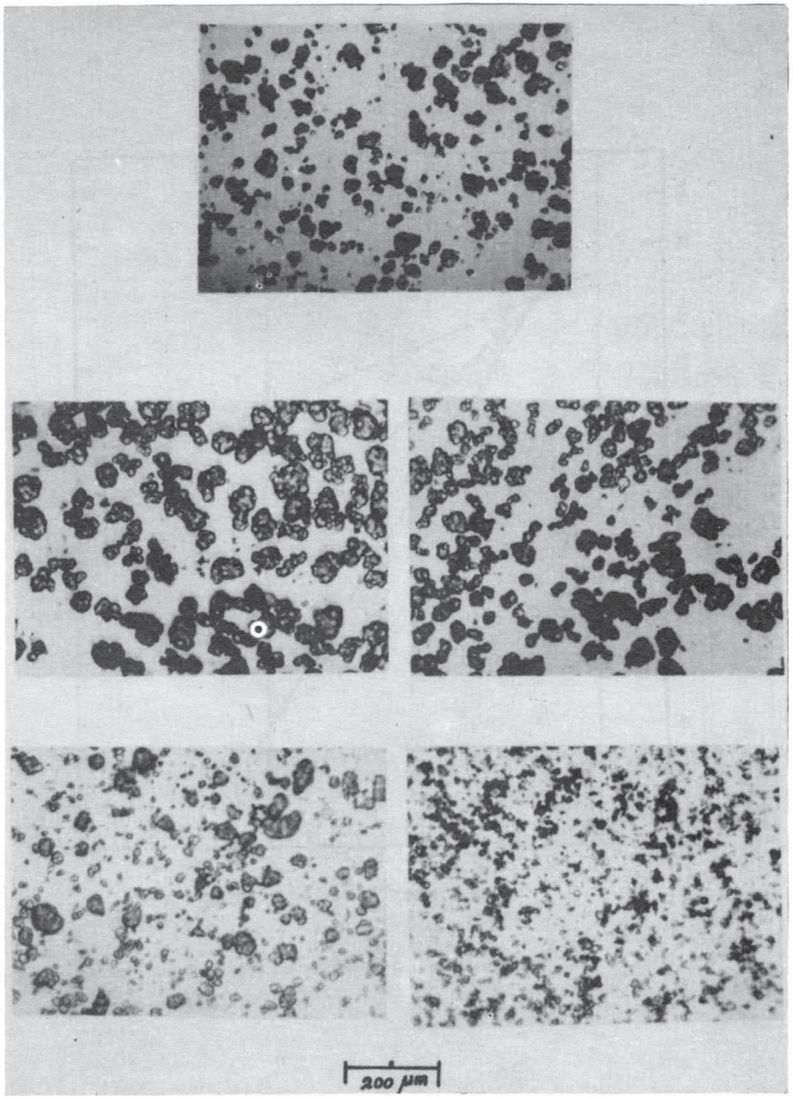

Fig. - 3 Effect of increased agitator power input on precipitation from fine seed of mixed particle size distribution.

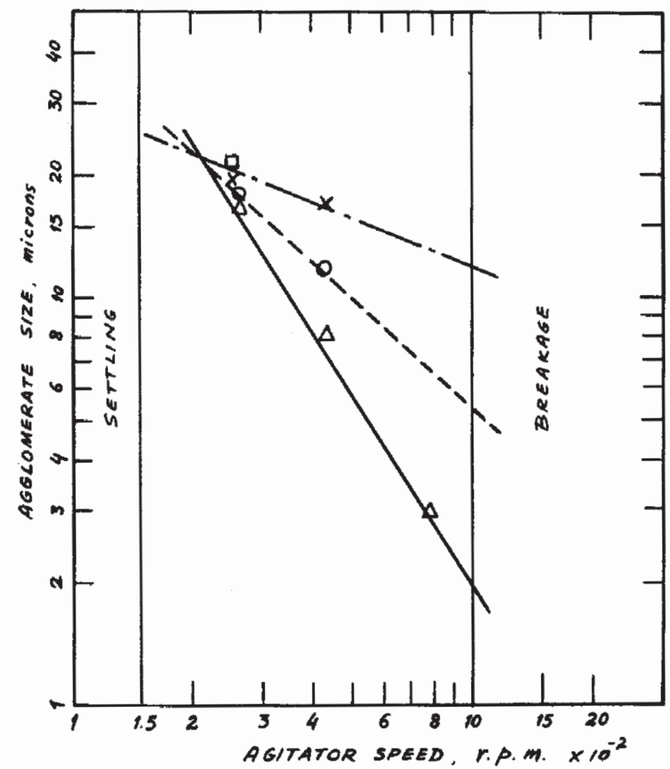

Fig. -4 Dependence of agglomerate size on agitator speed.

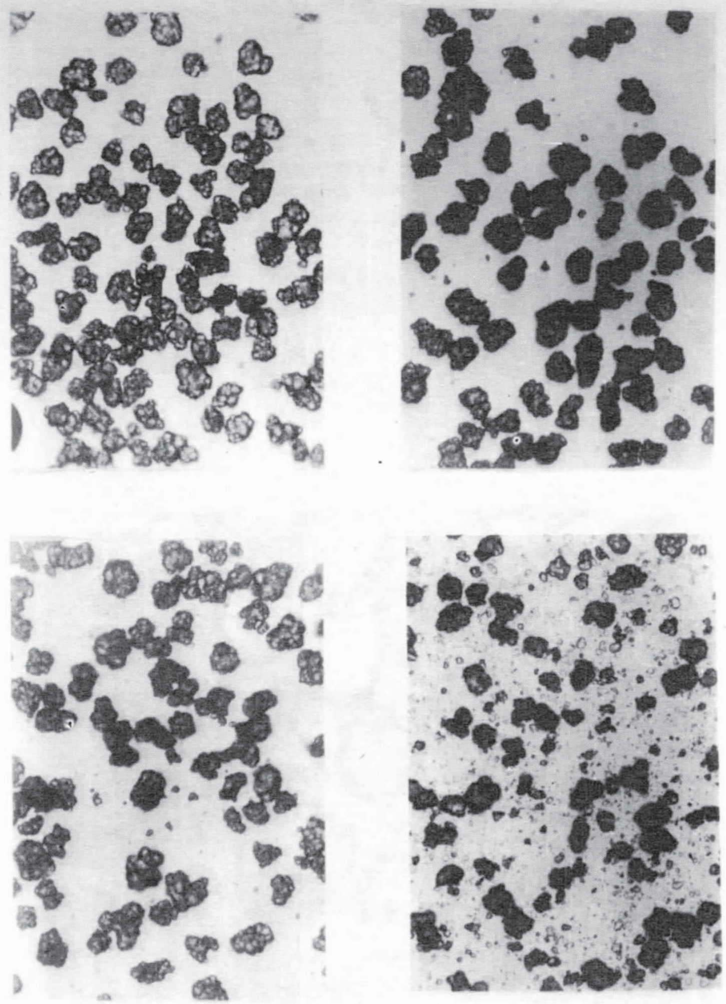

Fig. -5 Gross breakage of coarse seed at high agitator power input.

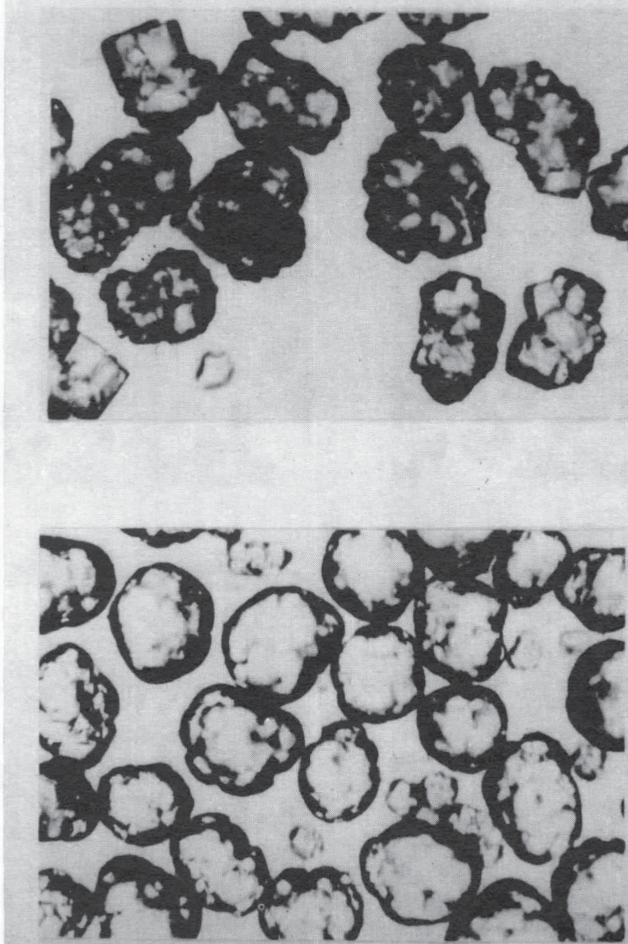

Fig. -6 Attritive erosion of large seed particles.

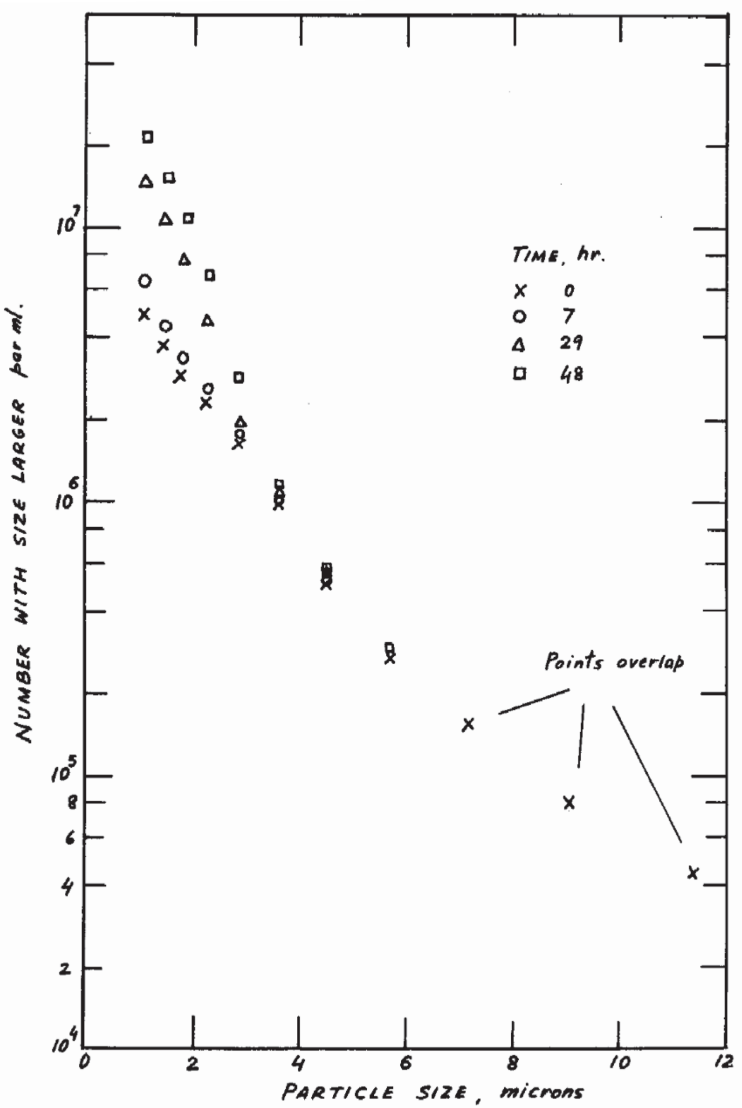

Fig.-7 Generation of small particles by attrition.