GIBBSITE GROWTH HISTORY - REVELATIONS OF A NEW SCANNING ELECTRON MICROSCOPE TECHNIQUE.

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Abstract

A new scanning electron microscope technique termed charge contrast imaging (CCI), unique to the Environmental SEM, has been developed at the Centre for Microscopy and Microanalysis. The technique enables the growth history of gibbsite particles from the Bayer process to be studied. The technique is used on uncoated polished sections. The seed gibbsite is clearly distinguished from freshly precipitated gibbsite enabling information on agglomeration and growth to be unambiguously obtained. Growth rings associated with each pass through precipitation are readily observed which enables the complete growth history of a particle to be ascertained; for example batch and continuously grown gibbsites can be distinguished. Growth of gibbsite on different crystal faces can be directly measured and the presence of secondary nucleation detected. The data obtained via this technique have been confirmed using specially prepared laboratory samples. The technique is now finding wider application in areas such as medicine (examination of kidney stones), mineralogy and ceramics.

Introduction

Imaging the internal structure of Bayer gibbsite particles to reveal how they grow has long been a goal for many people studying the Bayer process. Such particles grow by circulating through precipitation several times, either in batch or continuous reactors, and thus growth rings similar to growth rings in trees should form. The presence of such rings and possible methods to image them have been described previously (1). Techniques such as sectioning and differential etching had not been successful and the fine spacing was such that optical microscopy was an unlikely candidate. The use of laser confocal microscopy, although enabling a complete three dimensional picture of a hydrate particle to be constructed, gave no indication of possible growth rings (2). Electron-optic attempts focused on impurities such as calcia and iron which are precipitated immediately and thus could be ring markers. Unfortunately the small amount precipitated and the nanometre distance over which that precipitation occurs excludes techniques such as electron-microprobe analysis. Attempts have been made utilising the TEM as, with thin sections and some of the modern elemental analytical techniques, the potential does exist to achieve this goal. Consequently preparation of thin sections of the hydrate particles was attempted but their natural predisposition to cleave and their brittleness resulted in failure (a complete cross section of a particle was required). The alternative of calcining the material and then sectioning the alumina can be done successfully and that technique showed significant promise. However, when some of the possible analytical techniques were really put to the test, the claims somewhat outdid the results - sections of the now porous alumina particles are not the ideal samples for such cutting edge analytical work.

Another technique that had been pursued was the use of cathodoluminescence in the scanning electron microscope. This has the potential to analyse very low levels of impurities on polished sections at reasonable magnifications. It was at this stage that our interactions with Dr Brendan Griffin at the Centre for Microscopy and Microanalysis led to the technique which will be the subject of this paper. Dr. Griffin had been studying contrast obtained in uncoated non-conducting samples in the environmental SEM (ESEM) and had modified a detector to obtain relevant images. The images being obtained were not unlike some initial attempts at cathodoluminescence, except the picture quality was significantly better. A sample of Bayer gibbsite was examined and resulted in being an ideal test subject. Consequently special samples were prepared which helped rapid development of the technique, especially optimisation of the many process variables. This paper will describe verification of the technique which has been termed ‘charge contrast imaging’ (CCI) and illustrate the information that can be obtained from laboratory and Bayer refinery gibbsites.

The technique is applicable to most non-conducting materials and is now being used to examine a range of materials including: development and growth of kidney stones, zircon mineral growth and other minerals and ceramics, with ever increasing applications being found.

Charge Contrast Imaging (CCI)

The underlying physics behind the technique is not fully understood and is currently undergoing further investigation (with sponsorship by Alcoa). Readers are referred to the papers of Dr Griffin (3&4) and future papers if they wish to understand the technique more fully.
The technique essentially images an effect of charge build-up in uncoated specimens in the ESEM.

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

In conventional SEM, the charge build-up results in a flood of secondary electrons which normally causes saturation of the secondary electron detector preventing any imaging. However the ESEM, with its lower and variable vacuum in the specimen chamber, enables the charge dissipation to be controlled. Further, under very specific operating conditions, the emission from the sample is directly related to the trapped charge which in turn relates to the defect density. The defect density is a function of the type of crystal growth (eg initial nucleation as opposed to uniform deposition) and the amount of contaminants. Consequently the image shows high contrast across growth layers and where line defects, such as incipient or developed fractures, are present. It is now also considered that the impacting positive ions, which result from electron-chamber gas interaction, play a significant role in this imaging process and that the data is from the near-surface region of the sample. Such charge contrast has been made use of previously (accidentally). In the calcination of intermediate aluminas through to alpha alumina using a hot stage in the ESEM (2), the transformation was only observed because of charge contrast. Once the phase change was complete there was no charge contrast. However in that instance it was primarily a result of the microporous intermediate aluminas and the more dense alpha having different charging characteristics.

The gibbsite particles are mounted in a special resin to minimise edge charging effects and sectioned and polished to give a very flat surface, but with minimum distortion. The sectioned and polished samples are placed in the ESEM and illuminated by the electron beam which causes the particles to charge. The ESEM used has a specially modified detector to improve the secondary electron imaging. The atmosphere and other operating parameters are adjusted until the required CCI image is observed. The imaging is nowadays very rapid although first attempts were slow and image quality was poor. This was because of little understanding of the optimisation parameters such as pressure, operating voltage, beam current etc.. Use of laboratory prepared gibbsite samples with known structure such as thickness of growth rings enabled rapid improvement in imaging and image quality.

Gibbsite Structure - Verification of the Technique.

A polished section of a gibbsite sample which had been grown in the laboratory through six cycles from fine seed is shown in Figure 1 as imaged with CCI together with the normal SEM image. In the conventional SEM image, there is little detail with only grain boundary outlines and some defects being obvious. However for the CCI image a lot of internal structure is revealed, and specifically a series of concentric rings. The correct number of growth rings are evident.

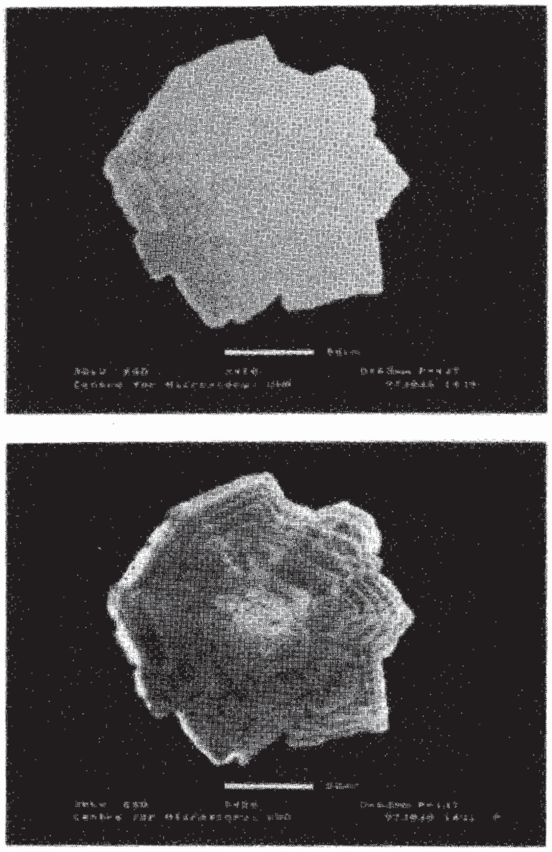

Figure 1 - Standard SEM and charge contrast images of laboratory produced hydrate.

The thicknesses of these growth rings are given in Table 1 together with the amount of growth put on the particle calculated from the yield and surface area. There is a one to one correspondence - the growth rings were being imaged. Also the seed gibbsite is readily distinguishable and that corresponds to the measured seed size. Even growth information about the seed material itself can be deduced (subsequently proven to be correct).

	Experimental	CCI measurement
	µm	µm
Seed size	45	45
growth ring 1	12	14
growth ring 2	3.6	3.2
growth ring 3	5.2	6.3
growth ring 4	4.9	4.4
growth ring 5	4.6	5.1
growth ring 6	4.5	5.1

Table 1 - Comparison of CCI and experimental data for the gibbsite test sample.

To determine whether some surface structure might be responsible for the image, samples were scanned using the atomic force microscope. A reasonably flat surface with no obvious ring structure was obtained and certainly no features corresponding to those observed by CCI.

From these observations and many further test samples with different numbers and thicknesses of growth rings and other known features, it was concluded that the growth structure was being accurately imaged.

Imaging of samples grown from both synthetic and plant liquors has been equally successful. Minor impurities such as calcia, silica and iron are not directly responsible for the major features observed although their contribution to, and enhancement of, some detail cannot be ruled out. Further work is in hand to relate the information observed to impurities or other causes for the observed contrast.

Growth Information

Rate of growth

Laboratory samples

As seen from Table 1 direct growth measurement can be obtained from the particles each time the sample is cycled between green and spent liquor. This can be a very accurate measurement provided due diligence is paid to the issues related to measurement on two dimensional sections of three dimensional particles (readers are referred to the numerous texts on such issues.) A more detailed image is shown in Figure 2.

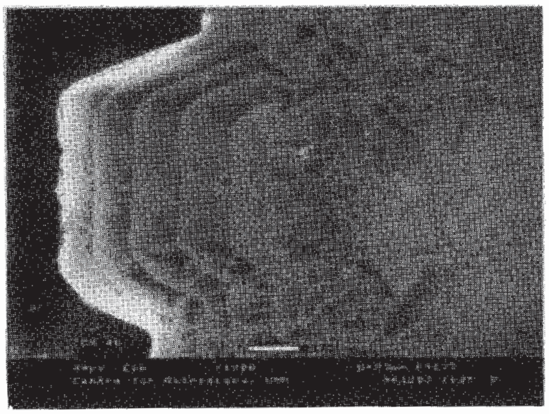

Figure 2 - Laboratory produced hydrate showing six cycles of growth.

Here it is possible to measure the growth rate on the different hydrate faces, ie in situ measurements for various faces grown under identical conditions. Determining the orientation of the face is not a trivial matter but it can be done by appropriate measurement of growth angles. A more elegant technique is to use Kikuchi patterns and that can now be done on areas as small as 1µm. Kikuchi patterns have been obtained on gibbsite (5).

Plant samples

Four samples from Bayer refineries are shown in Figures 3a-d.

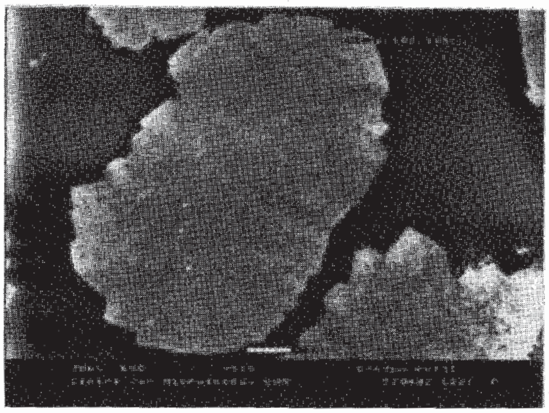

Figure 3a - Regular growth rings.

Figure 3a. There are regular growth rings, all essentially of similar thickness (allowing for increase in particle size). All particles for this sample showed such banding and similar thicknesses. This indicates that the particles have not only seen the same amount of growth in each cycle, but that all particles have had similar residence times and history which only occurs with batch precipitation systems. The growth rate is readily measured and that measurement should directly relate to the surface area of the seed and yield obtained. Importantly this demonstrates that the circulation of gibbsite particles from green to spent liquor in a plant scenario can be imaged just as well as the laboratory prepared samples.

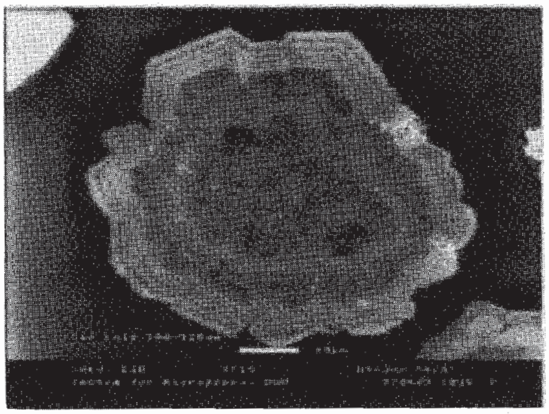

Figure 3b - Irregular growth rings.

Figure 3b. Pronounced growth rings of variable thickness are present. All particles showed such rings, but there was significant variation in thicknesses between rings. As the yield in each pass through a precipitation circuit is fairly constant, the major factor causing the variation in thickness will be residence time. Consequently this indicates that the sample is from a continuous system and that the particles have different residence times on each cycle around precipitation (particularly in the first few tanks where most of the growth occurs). Further it can be seen that the particle has grown from a small seed and that it is essentially a growth particle. (The latter information is also readily obtained via other techniques).

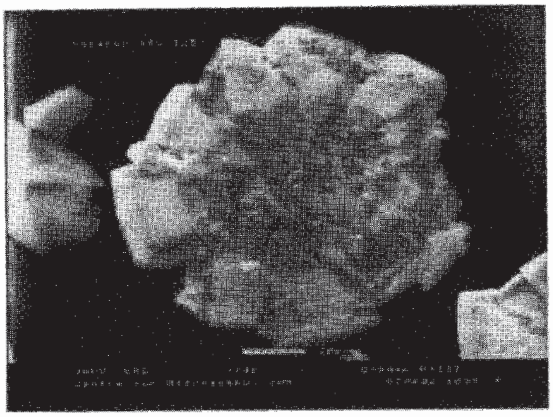

Figure 3c - Disjointed growth rings.

Figure 3c. The growth rings are somewhat disjointed. The particle has a notable three dimensional appearance. That is very typical in many of the images and it is often difficult to believe that a flat sample is being imaged. The cause of the disjointed nature of the rings is a consequence of the crystals intergrowing and that a section through a three dimensional particle is being viewed. Growth measurements can still be obtained but more caution is required as it is more difficult to ensure that a face perpendicular to the growth direction is being measured. The particle is a typical mosaic particle which is one with an agglomerated core of fine gibbsite particles surrounded by growth.

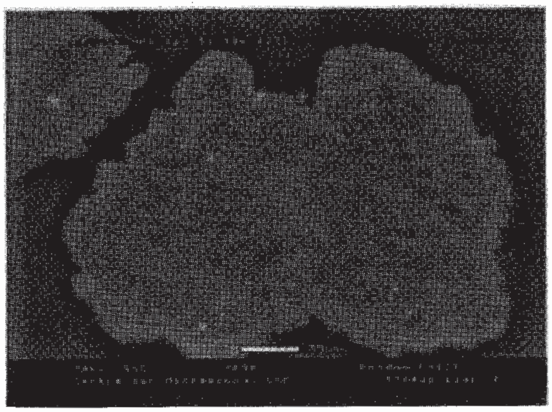

Figure 3d - No growth rings.

Figure 3d. The growth rings are almost absent indicating this particle has agglomerated and has not been around the circuit again after agglomeration. Within the agglomerated crystals themselves there is often banding indicating that some of the fine particles may have been around the precipitation circuit a few times before agglomerating.

Nature of growth

Prismatic crystals

In Figure 4 a prismatic crystal grown in a Bayer plant is shown together with the CCI image. The particle nucleus was a triangular shape which subsequently developed chamfers at the three corners and finally produced the normal hexagonal shape and the prismatic crystal. The thin banding indicates that the particle had many trips around precipitation, ie the particle was grown under low growth conditions. This change from a pyramidal to hexagonal structure is observed during secondary nucleation and growth on the external surface of hydrate particles.

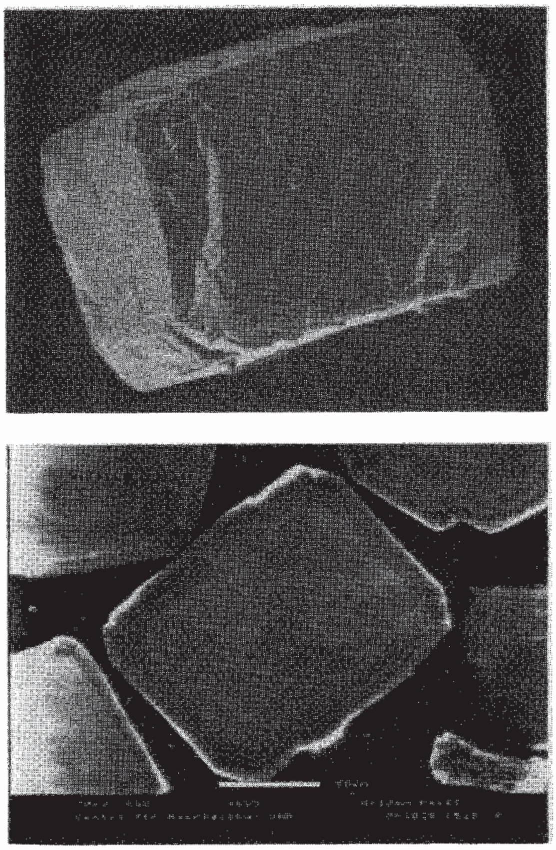

Figure 4 - Prismatic crystal - SEM and charge contrast image.

Agglomerates

The ability to distinguish seed particles from new growth makes the technique ideal for studying agglomeration. Examples are shown in Figure 5 where particles have agglomerated early or late in their history. It is necessary to re-emphasise that this is a section through a three dimensional particle and that it is possible to misinterpret such images as the particles may have joined together at an earlier stage than shown by these sections. However in one pass laboratory studies the information is unambiguous.

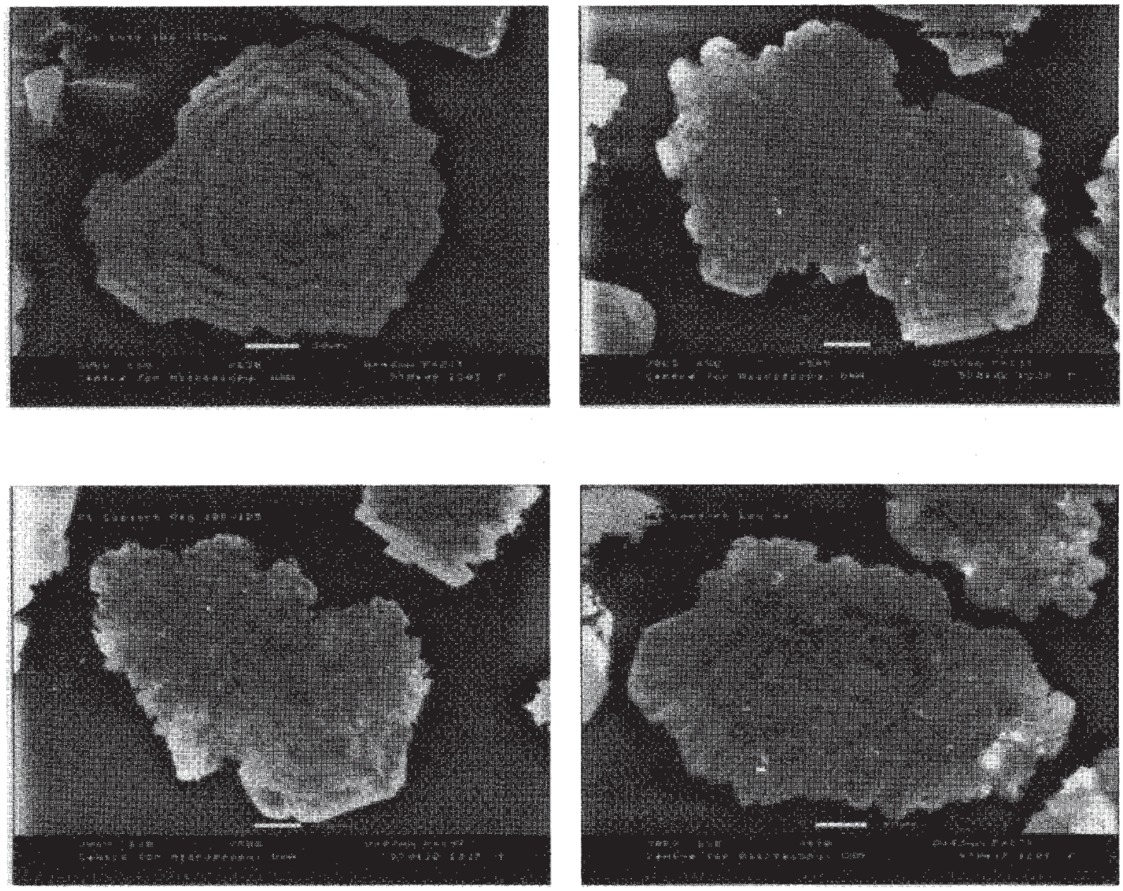

Figure 5 - Examples of particle agglomeration.

Nucleation

Much extra detail is incorporated in the growth bands. Close examination can indicate whether there has been secondary nucleation occurring. For seed gibbsite, which has been washed and dried, an induction period is frequently obtained. During that period fine features occur on the surface which eventually grow together to form a smooth surface. The progress of that can be seen with this technique, resolution now being obtained down to 100nm. The information directly matches that obtained using Field Emission SEM examination of the growing surface during precipitation.

Residence Time

As alluded to above, residence time information for particles can be obtained by this technique. For example, for samples from the first tank in a multi-stage continuous reactor system, the outer growth layer will directly relate to the residence time in that tank. Consequently measurement of the thickness of that growth layer enables the residence time of particles of different size to be determined and also for particles of the same size. Such information is critical in validating fluid dynamic type models of precipitators.

Further Applications

The technique, as it is continually being refined, is producing ever more and interesting information. For example in some samples there appears to be some fine rings within the main bands which may indicate significant changes within a single pass through precipitation (eg as might occur with inter-stage cooling or where there are large ratio drops between tanks in series). The technique has application in relating hydrate structure to such properties as hydrate toughness and its dissolution properties and good correlations are being found in these areas.

Conclusions

Charge contrast imaging is a powerful technique for studying gibbsite growth. The technique gives valid information on the growth history of gibbsite particles. It enables growth rates to be directly measured in the plant process. The technique should be an important adjunct to any studies related to gibbsite precipitation or studies on relating gibbsite morphology to its properties. Indeed it is proving to be an exciting and valuable tool in the study of any non- or semi-conducting material which has been grown.

References

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