ALUMINA AND HYDRATE - UNMASKING THEIR MYSTERIES, EIGHT YEARS ON

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ABSTRACT

At the Gladstone Conference in 1988 many of the techniques available to study the physical structure of hydrate and alumina and the distribution of impurities were presented.   Many new techniques are discussed and examples of the information that can be obtained are given. The low surface area of hydrate (<0.2 m^2/g) can now be measured using nitrogen B.E.T. Morphology analysis giving textural information can be obtained via a neural net system. Laser confocal microscopy gives three dimensional imaging of the inclusions within hydrate particles. Field Emission SEM is capable of resolving the fine pore structure (5nm) in alumina and enables low kV SEM for improved surface imaging to be used. Atomic force microscopy can give high resolution surface topography imaging as well as atomic resolution. Use of a hot stage in the Environmental SEM enables in situ observation of the calcination of hydrate particles.

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1.0 INTRODUCTION

Many of the techniques that are available for the examination of hydrate and alumina were discussed at the 1988 Alumina Quality Workshop (Roach et al, 1988). That paper also indicated the type of information which is required and the need to understand exactly what information is being sought and the ability of the equipment. For much of the information sought the equipment was not capable of providing the information. Since that time many techniques have developed further and new ones have emerged which allow some of that information to be obtained. In this paper the focus will be primarily on the morphology of hydrate and alumina. Equipment to study the nature and distribution of impurities in hydrate and alumina has also improved but there are significantly more sample preparation issues and particular care is required in interpretation of the data. There are also many surface analysis techniques which can be used to determine the chemical nature of the surface. Those techniques are beyond the scope of this paper.

2.0 HYDRATE

2.1 Surface area

The surface area of hydrate is a key property for predicting precipitation yield and controlling precipitation. An accurate measure of the surface area enables the specific rate constant for hydrate precipitation to be calculated with more certainty. Historically the surface area has been calculated from the size distribution of the hydrate which involves many assumptions, and the area calculated is at best only an approximation. The surface area is generally low, about 0.2 m^2/g, requiring krypton rather than nitrogen as the adsorbate when measured directly via B.E.T. gas adsorption; multi-point measurements are required which extends the analysis time considerably. New equipment now allows such low surface areas to be measured rapidly using multi-point with nitrogen adsorption. Some data are given in Table 1 and are compared to the previous values calculated from the sizing. There is not a one-to-one correspondence, a fact reflecting the much rougher surface of the smaller particles. Such equipment allows surface areas as well as sizing changes to be determined during precipitation. When combined with morphological examination, such data can give improved insight into the precipitation process, especially for agglomeration and the initial stages of hydrate precipitation.

Table 1
Surface areas of sized fractions of hydrate determined from laser sizing and B.E.T. measurement

Particle size (microns)	Laser Surface Area (m^2/g)	B.E.T. Surface Area (m^2/g)
150 - 130	0.013	0.016
90 - 150	0.020	0.036
45 - 90	0.033	0.085
- 45	0.130	0.350

2.2 External morphology

2.2.1 Image analysis.

Quantitative hydrate morphology data has long been a goal but unfortunately the many systems tested have not been capable of giving the range of information that can be obtained by the trained human eye. Standard image analysis computers still have problems of interpreting the textures of particles, something at which the eye is particularly adept. To overcome these

issues an image analysis system based on the use of neural networks was designed by the Centre for Intelligent Information Processing Systems at the University of Western Australia (Zaknich, 1996). The system was 'trained' with information on several thousand hydrate particles and has learnt to recognise and quantify several key features of the morphology. A typical analysis is given in Figure 1 for the hydrate shown. The system produces very repeatable results and is now more capable of distinguishing between hydrates than a trained operator and has the added benefit of providing quantitative data. Such information is vital in studies of hydrate strength and the effect of hydrate morphology on particle breakdown in calcination.

The potential exists to obtain such data with optical rather than electron-optic equipment. The use of deconvolution programmes to reduce distortions and blurring of optical images thus enhancing the depth of field may well allow such morphological analysis in the future without the need for expensive electron-optic equipment.
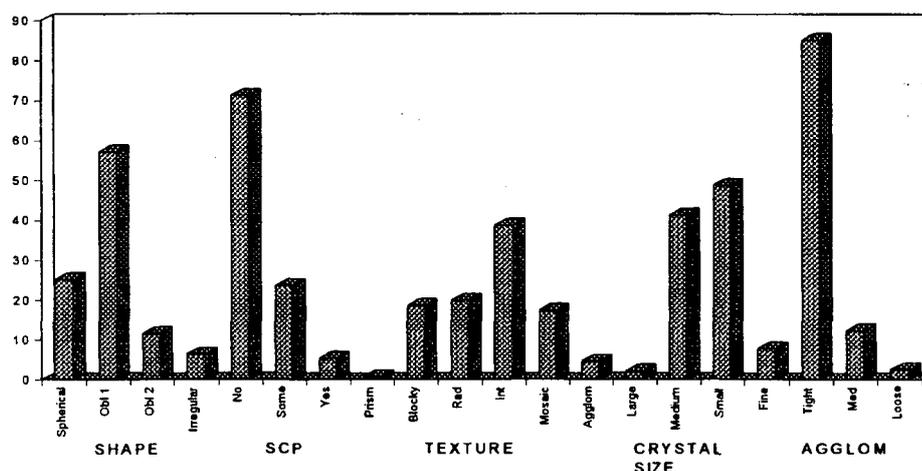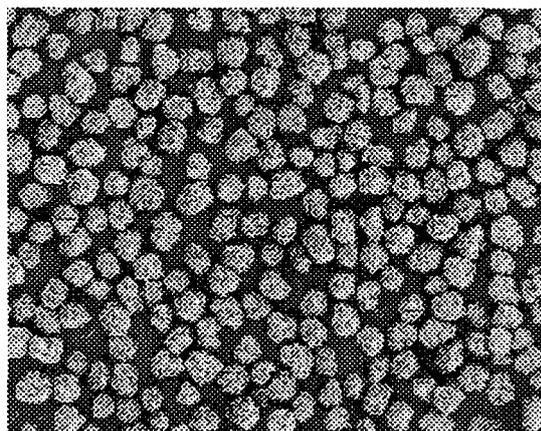

Figure 1   Sized Hydrate and the Morphology Analysis obtained using Neural Network program.

2.2.2   Field Emission Scanning Electron Microscopy

The scanning electron microscope (SEM) has provided excellent resolution of hydrate particles and has been the basic equipment for most morphology studies for the last 20 years. However the resolution of a standard SEM for non-conducting particles is limited. The latest Field Emission SEMs, which are now reasonably robust and easy to use, have the potential to give more morphological information. The field emission gun of the FESEM increases the potential resolution by over an order of magnitude. Also the low kV beam which can be used (typically <2kV) penetrates a much smaller depth into the surface and consequently gives much finer detail of the surface topography. An example of the resolution that can now be

achieved is shown in Figure 2. At such high magnifications the image must be interpreted with caution as even the fine texture of the coating material can be resolved, and could be mistaken for texture of the hydrate surface. Equipment is now becoming available that can operate at voltages as low as 0.2kV which eliminates the need to coat non-conducting materials. With a modern FESEM it is now possible to get resolution of about 2nm for hydrate particles. Such equipment can give an extraordinary amount of information and is especially useful for studying the initial part of the precipitation reaction.

2.2.3   Atomic Force Microscope

For even higher resolution than the FESEM the atomic force microscope (AFM) can be used. This equipment is developing rapidly and with features such as the use of tapping mode to reduce surface damage from the tip, detailed and valid information can be obtained. The difficulty is to ensure the particle of interest does not move and to place the tip of the microscope in the area of interest. A picture of a hydrate surface taken with an AFM is shown in Figure 3. At maximum resolution, atomic resolution is obtained. The AFM also enables quantitative measurement of the height of topographic features.

2.3   Crystal orientation

Hydrate (gibbsite) has an anisotropic structure and thus growth can vary on different crystal surfaces when the precipitation is controlled by the rate of chemical reaction at the surface. With a knowledge of the crystallographic structure it is possible to determine the various external faces on a hydrate particle from the angles between the crystal faces. Alternatively it could be possible to utilise information provided by the electron beam to do this by looking at the back-scattered Kikuchi patterns from the sample (Michael and Goehner, 1993). With modern computers and appropriate software programmes the orientation of a face from such signals can be quickly determined.

2.4   Internal structure

2.4.1   The laser confocal microscope.

One technique referred to eight years ago was the use of a refractive index oil such that the hydrate became translucent and thus the internal structure of the hydrate particle could be seen when viewed by optical transmission microscopy. Also mentioned was the potential of using a laser confocal microscope which would provide serial sections through the particle and thus, together with a large image analysing computer, enable three dimensional pictures of the internal structure of the hydrate to be obtained. This has been achieved and gives information on the distribution of impurity particles and cavities within the hydrate particle. The information generated is best viewed whilst rotating the image (via the computer) which enhances the three dimensional effect; a relevant video will be presented. Unfortunately many of the features of most interest are at or below the size of resolution of optical microscopy. Hence from a practical point of view, the laser confocal microscope offers little benefit for hydrate over standard optical microscopy or the use of either cut or polished sections.
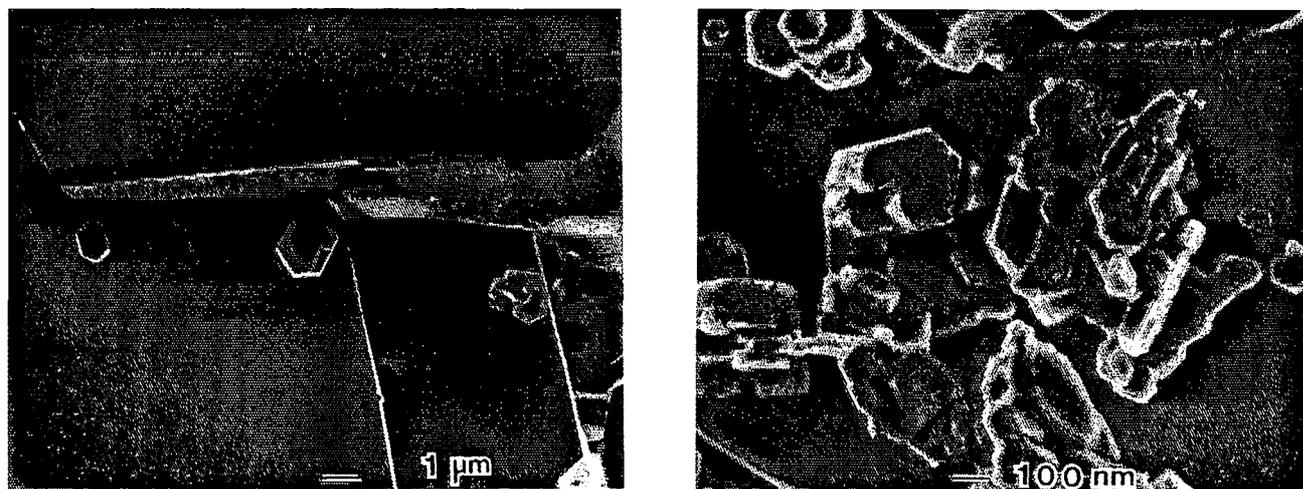
Figure 2.   Field Emission SEM micrographs of the surface of hydrate particles.
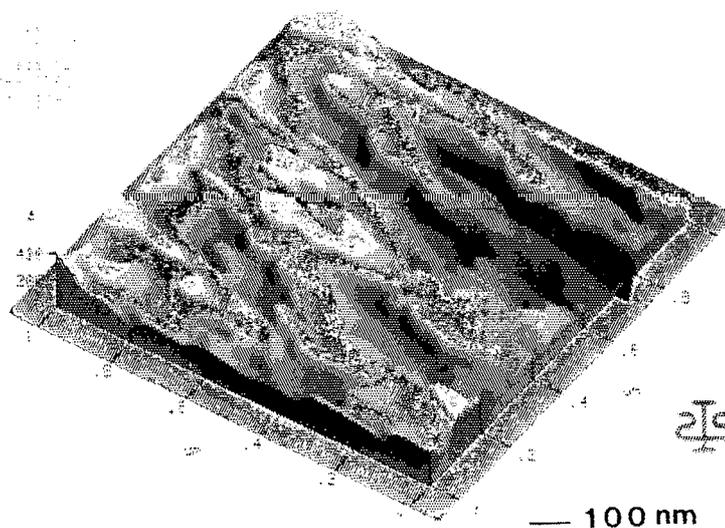

— 100 nm

Figure 3.   The surface of the basal plane of a hydrate particle imaged using   an atomic force microscope.

However, examining the fluorescence image from the confocal microscope provides interesting data. The particles fluoresce because the wavelength of the laser (480nm) is similar to that needed to activate many of the organics in the particle. A video taken using fluorescence showing a series of sections through a particle will be presented and indicates interesting distributions of fluorescence (and thus presumably organics) within hydrate particles.

2.4.2   Polished and cut sections.

Detailed examination of the internal structure utilising the various electron optic instruments or the atomic force microscope requires the use of either polished, cut or broken sections. There are inherent difficulties in sample preparation especially because of the susceptibility of hydrate to cleave so readily. Also judicious choice of polishing, cutting and etching procedures is required relevant to the features to be observed. However such techniques, including the use of thin sections mentioned eight years ago, can potentially give all the information required on the internal structure. Further information could be obtainable by adding tracers during the precipitation process or use of natural impurities if they possess cathode luminescence.

There is now little limit to observing the hydrate surface or internal structure. Information from the macro, through to micro and even at the atomic size can be obtained. The next stage is the use of microscopes in in-situ growth experiments. That can be achieved with both optical microscopy and with the atomic force microscope and will provide further stimulating and important information on the crystallisation process. In conducting such work it is essential that an experimenter has a full understanding of the capabilities and manner of working of the equipment. It is simpler to design the experiment so that the features of interest are easy to observe with the equipment rather than to do the experiment and hope that today's range of expensive equipment can 'show you something'.

3.0   ALUMINA

3.1   Surface examination

When hydrate is calcined to alumina the surface area increases rapidly to around $400m^2/g$ and then drops down to the desired value of about $75m^2/g$. This is consistent with an internal structure which initially contains pores of a few nanometres in size which then grow to about 15nm. SEM imaging of alumina could not resolve such pores and they could only be resolved by examining thin sections with the TEM. In Figure 4 the surface of alumina is shown at two magnifications. At the higher magnification and resolution available with the FESEM the fine pore structure of the alumina is readily distinguished. Pores as fine as 3nm have been resolved.

Extra information is obtained on the inter-particle variations in properties such as surface area and pore size distributions as these are normally bulk measurements. However it is necessary to interpret surface information cautiously when trying to relate it to the internal structure. Examination of sections is the preferred method to obtain such information.

3.2   In situ calcination.

The ideal would be to calcine a particle and observe the changes within the microscope. This can be achieved using the Environmental SEM which allows reasonably high pressures to be accommodated in the chamber. Using a hot stage the hydrate can be calcined to alpha alumina. A video of the transformation will be presented. The progress of the transformation is shown in Figure 5 with the alpha forming first on the edges and corners of the hydrate. The hot stage also enables the development of the large cracks in normal calcined alumina to be observed. Indeed the ESEM with a hot stage becomes a miniature laboratory; the water vapour pressure during the calcination process can even be controlled. Unfortunately the resolution of the equipment is only similar to a conventional SEM.

4.0   IMPURITIES

Various techniques were mentioned eight years ago which had the potential to provide specific information on the nature and distribution of impurities in hydrate and alumina. For impurities on the surface there are many surface analysis techniques which have been used, and have continued to be applied because of the interest in the reaction at the surface in hydrate precipitation.

For impurities throughout the particles the challenge is still to obtain good thin sections for analysis as the impurities generally are distributed in fine bands within the hydrate. The equipment to measure such impurities is now so refined that resolution down to 1nm is claimed by many equipment manufacturers using high resolution TEM/EDS equipment. Such resolution would readily detect the impurity bands of calcia, iron and silica discussed in Roach et al 1988.

There are many other techniques which have the potential to give the information on impurities which would enable the impurities to be used as growth markers. Perhaps it will be possible to watch the impurities migrate as the hydrate is calcined - thin sections of hydrate can readily be calcined by the electron beam itself.
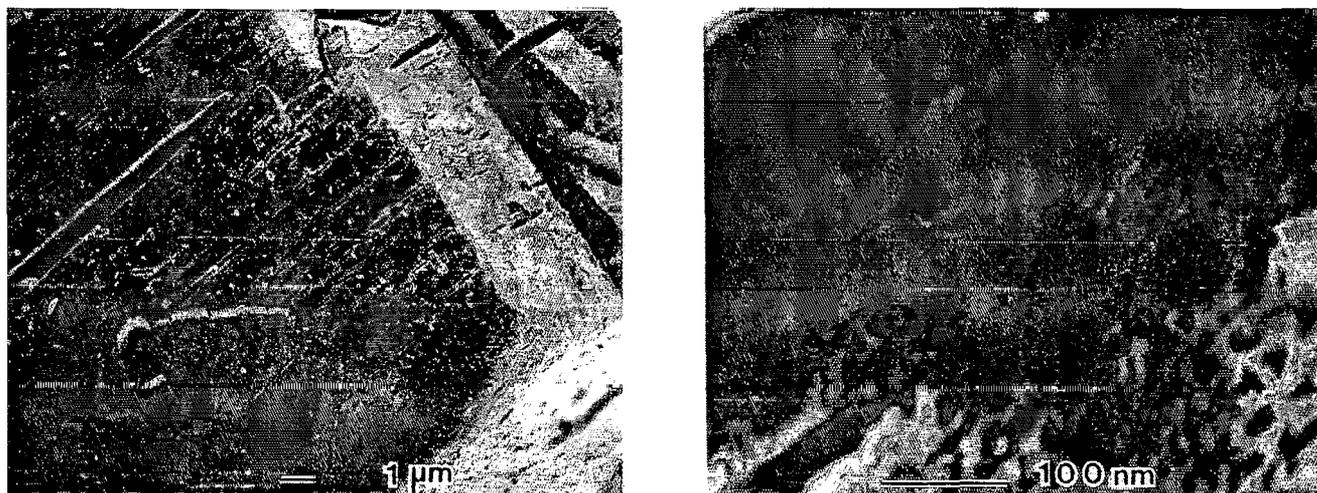

Figure 4.   Field Emission SEM micrographs of the surface of smelter-grade alumina. At the higher magnification the small pores in the alumina can be distinguished.
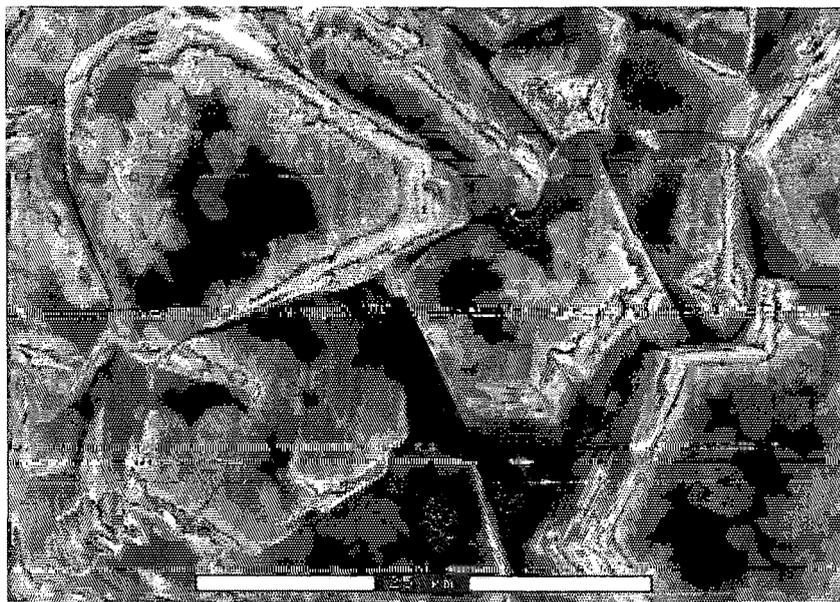
Figure 5.   The transformation of intermediate aluminas to alpha alumina taken using a hot stage in the
Environmental SEM. The alpha alumina can be seen growing from the corners and edges into the
particle.

5.0   CONCLUSIONS

The techniques available for examination of hydrate and alumina continue to evolve and provide
improved insights into the basic mechanisms of the processes of interest such as hydrate agglomeration,
secondary nucleation and calcination. The capability of modern personal computers has been the
catalyst of many of these developments and the image enhancement afforded by such computers
continues to improve the resolution of the equipment. Also such computer processing power enables
much of the information to be quantified. That will assist in seeking correlations between factors such
as hydrate morphology and particle strength. The potential use of some of these techniques in in-situ
growth experiments and in calcination studies promises to lead to a complete understanding of
processes such as induction periods and secondary nucleation in hydrate precipitation. Obtaining
information on the nature and location of the impurities in hydrate and alumina is still a challenge;
relevant equipment is available but suitable sample preparation techniques have yet to be perfected.

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