

## MORPHOLOGICAL INVESTIGATION OF SODIUM OXALATE CRYSTALS GROWN IN AQUEOUS SODIUM HYDROXIDE SOLUTION

Weng Fu, James Vaughan

The University of Queensland, School of Chemical Engineering, Level 3, Chemical Engineering Building (74), College Road St Lucia, Queensland 4072 Australia

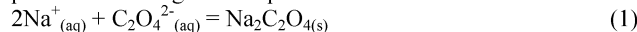
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### Abstract

Sodium oxalate crystals grown in aqueous sodium hydroxide solutions with different concentrations were characterized by optical and atomic force microscopy to examine their morphologies. Experimental results indicated that a high concentration of sodium hydroxide had a dramatic effect on reducing the size of sodium oxalate crystals. A nitrogen gas adsorption technique was employed to quantify the change of specific surface area of sodium oxalate. A two dimensional image analysis technique was also employed to estimate surface area and the crystal size distribution of sodium oxalate.

### 1. Introduction

Of the many organic compounds present in Bayer liquor, sodium oxalate is known to have one of the most detrimental effects on the gibbsite precipitation process [1]. Sodium oxalate precipitates out in the cooler end of the precipitation circuit of the Bayer process according to the equation:



This is because the equilibrium solubility of sodium oxalate can be decreased by reducing the temperature [2]. Such precipitation of sodium oxalate, in turn, results in numerous industrial problems such as increasing the content of gibbsite fines [3], decreasing gibbsite agglomeration efficiency [4], increasing the formation rate of oxalate-gibbsite scale [5] and increasing the residual soda in alumina products [6]. These problems can be attributed to the morphological variability of sodium oxalate crystals. Although oxalate tends to form monoclinic crystals, the morphology of oxalate crystals grown under industrial Bayer conditions is highly variable. Crystal morphology includes individual needles, and needle clusters which resemble fans, bow-ties and ball-like structures [7]. Despite the important industrial implications of this process, the origins of this morphological variability are poorly understood because many variables in the industrial Bayer solutions such as sodium hydroxide concentration, inorganic impurity species and organic species may influence the morphology of oxalate crystals. Therefore, the objective of this research is to establish the effect of sodium hydroxide concentration on the size and morphology of sodium oxalate crystals.

### 2. Experimental

#### 2.1 Precipitation of Sodium Oxalate

All chemicals were of analytical grade and used without further purification. According to the solubility data of sodium oxalate in water [8], saturated sodium oxalate solution was prepared at 55°C, then left to cool to 20 °C, leaving a supersaturated sodium oxalate

solution. The relative supersaturation of this solution ( $\sigma = (c - c^*) / c^*$ ) is 0.36, where  $\sigma$  is relative supersaturation,  $c$  and  $c^*$  are concentration and equilibrium concentration, respectively. A series of sodium hydroxide solutions with different concentrations were prepared (shown in Table 1). The experimental procedure consists of pumping 50 mL of supersaturated sodium oxalate solution into 100 mL of the sodium hydroxide solutions at a rate of 10 mL/min. The mixed solution was stirred with an axial flow hydrofoil impeller at 300 rpm to provide gentle agitation. Crystals produced were left to stir for further 60 minutes, filtered and washed with absolute ethanol, then stored for characterization. The experiments were carried out at 20°C. For comparison, sodium oxalate crystals grown in 0 mol/L sodium hydroxide solution were also precipitated from 0.34 mol/L supersaturated sodium oxalate solution at 20°C, after a two-day induction period.

Table 1 The parameters for the effect of sodium hydroxide on the precipitation of sodium oxalate

Parameters	Supersaturated Sodium Oxalate Solution	Sodium Hydroxide Solutions
Solution concentration, mol/L	0.34	2.5; 5; 7.5; 10; 12.5
Solution volume, mL	50	100

#### 2.2 Characterization

Surface area of sodium oxalate crystals was measured by nitrogen gas adsorption. Samples were first degassed overnight to pressures of ~2 Pa at 200 °C in a Micromeritics VacPrep061, prior to analysis with a Micromeritics Tristar 3200 gas adsorption instrument.

Optical images were collected in air using an OLYMPUS BX61 optical microscope. AFM images were obtained in air using a MFP-3D atomic force microscope (AFM) (Asylum Research, USA) in AC mode with triangular silicon nitride cantilevers.

#### 2.3 Image Analysis

Particle size measurement techniques based on laser diffraction have known limitations for anisotropic particles because the laser diffraction technique is strictly valid for spherical particles. Due to the needle shape of sodium oxalate crystals, the measured particle diameter of an equivalent sphere is dependent on the orientation of the particle as it passes through the laser beam [9]. Therefore, a 2-D image analysis technique is employed to estimate crystal length and width.

This image analysis procedure begins by spreading sodium oxalate crystals onto glass slides to obtain optical microscopy

images. Secondly, UQ Hydrometallurgy Image Analysis (UQHIA) software was used to convert the optical images to binary based on a user-selected threshold. Optimal threshold was determined through comparison of the binary image with the original image. The identified crystals were then analysed for their projected 2D surface area and length based on the image scale (Fig 1).

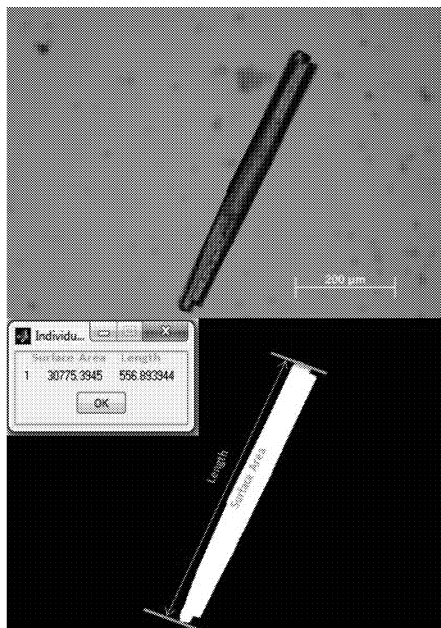


Figure 1 Principle of UQ Hydrometallurgy Image Analysis software

Based on the primary data, the crystal width was calculated as the projected area divided by length. Thirdly, this method assumes that the width is equal to the height. From this assumption, the volume, mass and specific surface area for identified crystals was estimated. The particle size distribution was also obtained. In order to obtain statistically meaningful data, more than 1,000 crystals were analysed for each sodium oxalate sample.

### 3. Result and Discussion

#### 3.1 Effect of sodium hydroxide concentrations

The morphology and size of sodium oxalate crystals resulting from crystallization experiments were evaluated. Optical microscopy results (Fig. 2) demonstrate that acicular sodium oxalate crystals grown from sodium hydroxide solution are much smaller than those obtained under the same conditions from aqueous solution. This result provides evidence that a high concentration of sodium hydroxide has a dramatic effect on reducing the size of sodium oxalate crystals. A possible mechanism for this observation is that the supersaturation of sodium oxalate in the synthesized Bayer liquor increases by the increasing the concentration of sodium ion, resulting in an enhancement of the driving force of the precipitation which leads to the reduction of the crystal size.

The typical concentration of sodium ion in industrial Bayer liquor is in the region of 6-7 M [10]. As shown in Fig. 3, the measured specific surface area of oxalate crystals increases dramatically at sodium hydroxide concentration above ~ 4 M. This large amount

of additional surface area could provide more sites for secondary nucleation of gibbsite in the Bayer process.

Compared with sodium oxalate crystals grown without additional NaOH, the root mean square roughness (RMS) of {110} faces of sodium oxalate crystals grown in sodium hydroxide solution is much higher (Fig 4). The high concentrations of sodium hydroxide solution may modify the solution interfacial tension, reduce the interfacial free energy and cause a surface roughening effect along a specific crystallographic direction. Additionally, the increased specific surface area of oxalate crystals grown in high sodium hydroxide solution could also result from the increased surface roughness.

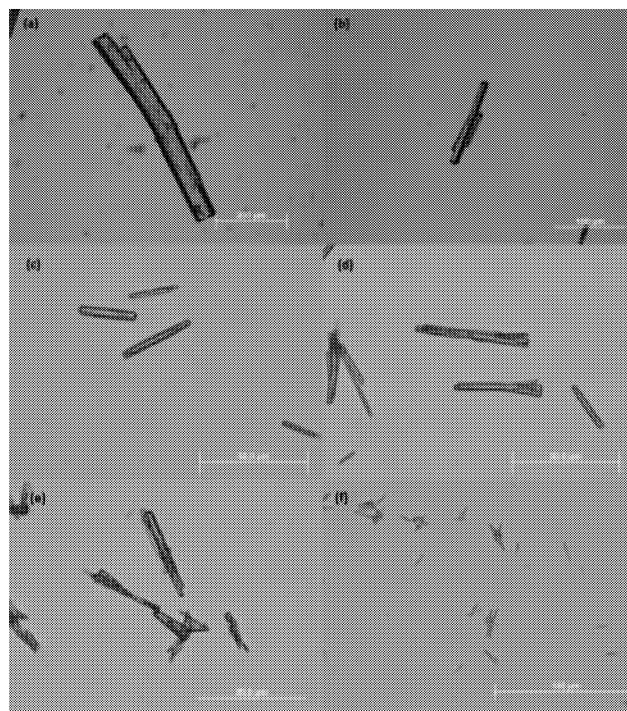


Figure 2 Sodium oxalate crystals grown under different concentrations of sodium hydroxide. The NaOH concentration sequence is (a) 0 mol/L, (b) 1.67 mol/L, (c) 3.33 mol/L, (d) 5 mol/L, (e) 6.67 mol/L, (f) 8.33 mol/L.

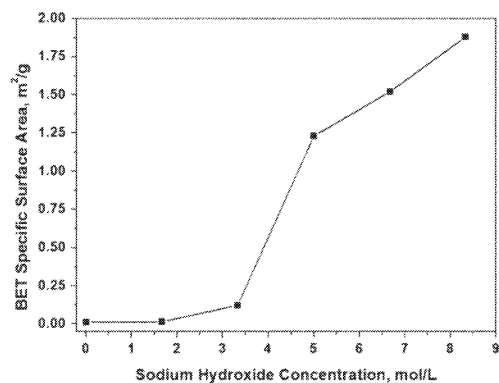


Figure 3 BET specific surface area of sodium oxalate crystals grown under different concentrations of sodium hydroxide. The NaOH concentration sequence is 0 mol/L, 1.67 mol/L, 3.33 mol/L, 5 mol/L, 6.67 mol/L, 8.33 mol/L.

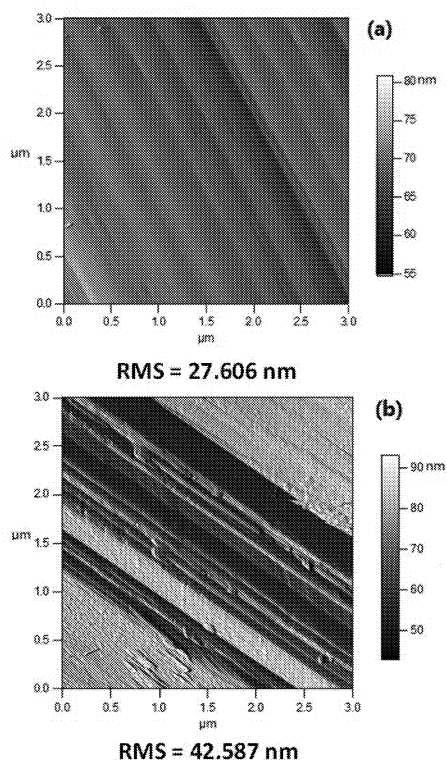


Figure 4 AFM images of the {110} faces of sodium oxalate crystals grown in (a) 0 mol/L, (b) 1.67 mol/L NaOH solution.

### 3.2 Image Analysis

The calculated specific surface areas obtained by image analysis follow the same trend as the measured specific surface area by nitrogen adsorption (Fig. 5). The deviation between the calculated and measured specific surface area is large for low surface area crystals because the number of nitrogen molecules unadsorbed in the void volume of the nitrogen adsorption cell at such low surface areas ( $<1 \text{ m}^2/\text{g}$ ), can be large compared to the number of molecules adsorbed on the surface, contributing to a measurement uncertainty. However, the two values for high surface area crystals ( $>1 \text{ m}^2/\text{g}$ ) are in close agreement and provide validation of 2-D image analysis technique as a way of estimating the surface area for these types of sodium oxalate crystals.

The particle size distribution in terms of length of crystals is summarised in Fig. 6. Sodium oxalate crystals with low specific surface areas ( $<1 \text{ m}^2/\text{g}$ ) exhibit very broad crystal length distributions in the region of 0-250  $\mu\text{m}$  in Fig.6(a). In contrast, the length distributions for high-surface-area oxalate ( $>1 \text{ m}^2/\text{g}$ ) is relatively narrow from 0 to 50  $\mu\text{m}$  in Fig.6(b). For oxalate crystals grown in 6.67 M NaOH solution, there is small peak at the length of 3  $\mu\text{m}$ , indicating that high concentration of sodium hydroxide solution reduces the oxalate crystal size.

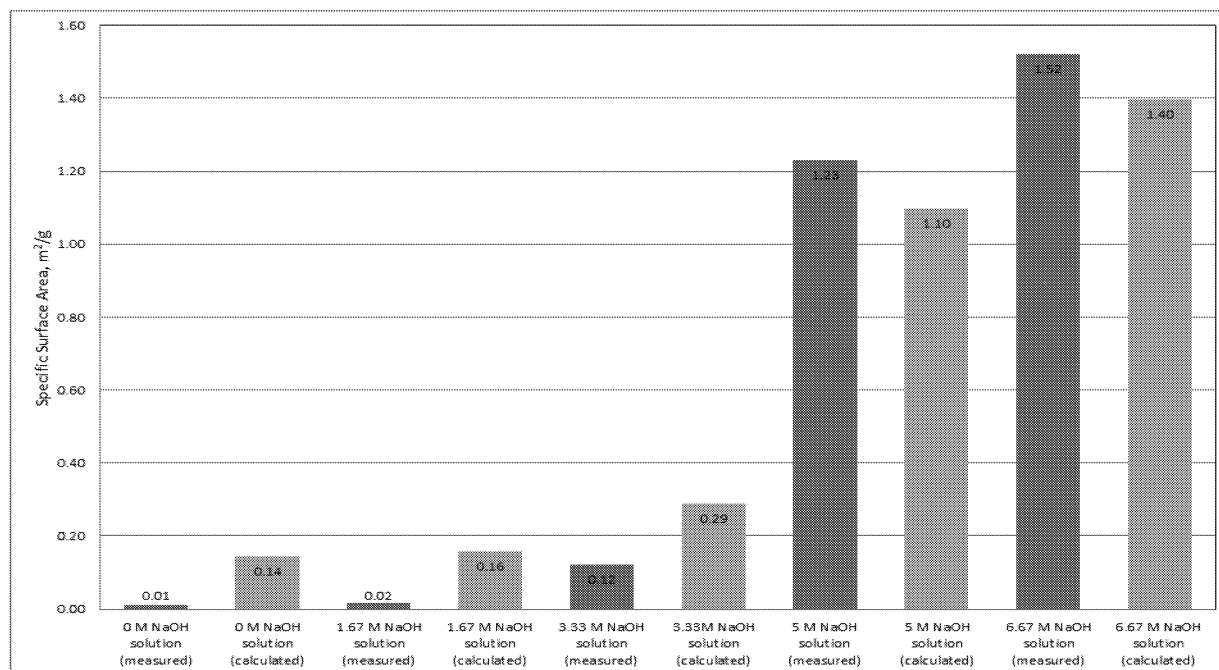


Figure 5 The comparison of measured specific surface area of sodium oxalate crystals and calculated surface area using image analysis technique.

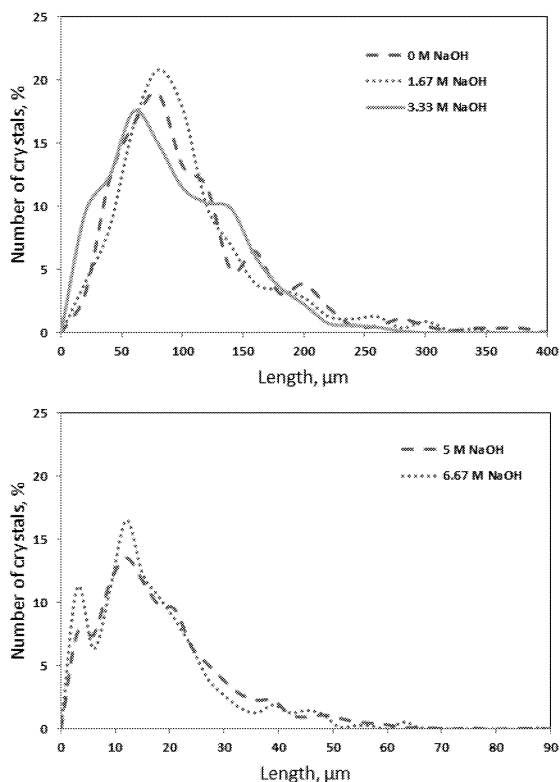


Figure 6 The particle size distribution of sodium oxalate crystals grown under different concentrations of sodium hydroxide. The NaOH concentration sequence is (a) 0 mol/L, 1.67 mol/L and 3.33 mol/L; (b) 5 mol/L, 6.67 mol/L.

#### 4. Conclusion

Our data provide evidence that high concentrations of sodium hydroxide solution during sodium oxalate crystallization had a dramatic effect on reducing the size of sodium oxalate crystals. The root mean square roughness (RMS) of {110} faces of sodium oxalate crystals grown in sodium hydroxide solution is higher than those grown in water. An image analysis technique yielding sodium oxalate surface area was validated by comparison with gas adsorption results. The image analysis results showed that oxalate crystals with low surface areas (<1 m<sup>2</sup>/g) exhibit very broad crystal length distributions in the region of 0-250 μm, while the length distributions for high-surface-area oxalate (>1 m<sup>2</sup>/g) is relatively narrow from 0 to 50 μm.

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