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Selective molecular weight adsorption from polydisperse polysaccharide depressants

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ABSTRACT

Guar and carboxymethyl cellulose (CMC) polysaccharides play an important role in the mineral processing industry as gangue depressants in the flotation process. As with all polymers, they are polydisperse molecules, exhibiting a range of molecular weights about a mean. Thus, the aim of this study was to determine whether there is competitive adsorption between chain lengths of different molecular weights and to determine which chain lengths adsorb preferentially. Gel permeation chromatography (GPC) was used to assess the molecular weight distribution of guar and CMC depressants of low and high molecular weights, before and after adsorption onto a talc substrate. The depressant solutions were allowed to react for increasing periods of time and the change in the molecular weight of the adsorbed fraction over time was assessed. Equilibrium adsorption isotherms and cryogenic scanning electron microscopy were utilised to complement the GPC data.

It was found that the shorter chain lengths of the high molecular weight depressants adsorbed preferentially. The kinetics of adsorption were rapid and the molecular weight of the adsorbed fraction did not change substantially thereafter. This was contrary to most of the literature which suggests that the shorter chain lengths will diffuse rapidly to the mineral surface and adsorb, but will be replaced by the longer chain lengths over time due to favourable changes in entropy. An explanation is offered in terms of a greater dependence on adsorption energy in the case of this system. The low molecular weight depressants adsorbed more evenly across the entire molecular weight range, but still showed some preferential adsorption of the shorter chains. The implications for the flotation industry are discussed.

1. Introduction

Polysaccharide depressants, guar and carboxymethyl cellulose (CMC), play an important role in the selective separation of unwanted gangue minerals from the valuable minerals in the South African platinum mining industry. Polymeric depressants reduce the hydrophobicity of floatable gangue minerals, rendering these particles hydrophilic and resulting in an upgraded concentrate. Guar and CMC depressants are both made up of simple sugars (galactose and mannose) joined in a branched configuration. The principle difference between a CMC and a guar depressant is that CMC's carry charged carboxylate groups, described by the degree of substitution, while guar depressants are relatively neutral molecules. In order for a CMC depressant to be an effective depressant, the negative charge must be shielded by positively charged cations present in the solution (Parolis et al., 2008).

As with any polymer, depressants are polydisperse, meaning that they are made up of polymers of different chain lengths, usually normally distributed around a mean. As the distribution approaches a uniform chain length, the polydispersity approaches unity. The effect of molecular weight of depressants on the depression of floatable gangue has been investigated by McFadzean et al. (2011) where they found that the low molecular weight depressants were better depressants of naturally floatable gangue at typical plant dosages. However, since the depressants were polydisperse and there would be competitive adsorption between chains of differing lengths, it was not known in this study precisely which chain lengths were adsorbing. Previous studies have shown that, in a mixture of polymers of different chain lengths, the polymer of low molecular weight will be adsorbed first, but will subsequently be displaced by the polymer of longer chain length (Felter and Ray, 1970; Kawaguchi, 1990). This is due to the diffusion rate of short chains being greater than that of long

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chain polymers. However at longer times, adsorption of the longer chains is favoured since these lose less translational entropy (per unit mass) in the solution, while they gain approximately the same (total) adsorption energy (Fleer et al., 1998). Janardhan et al. (1990) found that this was not always the case and that the type of molecular weight species adsorbed onto TiO_2 was dependent on the concentration. At lower concentrations, low molecular weight species were displaced by higher molecular weight species. However, at high concentrations the reverse was true. These authors attributed this to the fact that at high concentrations, the adsorption energy contributes more to the total free energy. However, Lipatov et al. (2008) attributed this phenomenon to the formation of macromolecular clusters at higher concentrations that blocked the transfer of higher molecular weight fractions from the surface. Devotta and Mashelkar (1996) present a model for the adsorption–desorption process of a bimodal distribution of polymer chain lengths onto both a porous and non-porous surface. Both models predict that the high molecular weight polymer will eventually displace the low molecular weight polymer, only the rates will differ. This is due to the gradual blocking of pores on the porous surface by the shorter chain polymers and the subsequent slow disengaging of these shorter chains and the slow diffusion of the longer chain lengths into the pores. However, one of the assumptions for this model was that the pore radius was large compared to the radius of gyration of the longer chains. This may not necessarily always be the case. Kuratara et al. (1993) found that, in certain cases when the larger molecule cannot easily penetrate into the silica pore without significant deformation, the smaller chain length in a binary mixture of polystyrene will adsorb preferentially.

The objective of this paper is to determine which chain lengths in a polydisperse CMC and guar depressant preferentially adsorb onto a floatable mineral such as talc. This was tested for both high and low molecular weight CMC and guar depressants and the implications for flotation are discussed.

2. Experimental details

2.1. Talc

Talc from Balmat, New York, was purchased from Wards Natural Science Establishment. It was pulverised in a ring pulveriser for 2 min and then wet-screened on a 38 μm sieve. The surface area of the sub-38 μm size fraction was found by BET analysis to be 13.0703 m^2/g.

2.2. Depressants

The depressants were obtained from Senmin Pty (Ltd). These consisted of two CMC's with molecular weights of 34,300 and 854,000 g/mol and degrees of substitution of 0.68 and 0.81, respectively. The two guars had molecular weights of 38,300 and 981,000 g/mol, respectively. The characterisation of depressants for molecular weight, purity, and percent insoluble material was done using standard techniques. Table 1 shows the characterisation data for all four depressants.

Table 1
Depressant characterisation.

	Moisture (%)	Purity (%)	Insoluble material (%)	Molecular weight (g/mol)	Degree of substitution
Low MW CMC	10.96	92.88	No insolubles	34 300	0.68
High MW CMC	13.44	98.16	No insolubles	854 000	0.81
Low MW guar	13.21	96.85	4.80	38 300	–
High MW guar	13.61	96.18	19.83	981 000	–

2.3. Matrix solution

The ionic strength of all experiments was maintained constant at 1×10^{-2} mol/L by adding $Ca(NO_3)_2{\cdot}4H_2O$ to deionised water. The Ca^{2+} ions performed the added task of shielding the ionic charge on the talc and assisting in the CMC adsorption by masking the negatively charged carboxyl groups. The pH of the depressant solutions was adjusted to pH9 using dilute sodium hydroxide solution.

2.4. Experimental procedure

2.5 g of New York Talc was accurately weighed into an Erlenmeyer flask and conditioned in 50 ml of 0.808 g/L depressant solution in a shaker bath at 25 °C for time intervals: 5 min, 15 min, 30 min, 2 h, 6 h, and 24 h. Each solution was then centrifuged for 10 min at 5000 rpm and the supernatant decanted off. This residual depressant in the supernatant solution was concentrated by evaporating off the liquid through freeze drying. A sample of depressant before adsorption (0 min) was also freeze dried as a reference sample. After freeze drying, the molecular weight of the samples was determined by gel permeation chromatography (GPC). The samples were dissolved in 10 ml of 0.2 M $NaNO_3$ eluent, filtered through 0.45 um filters and injected into a waters ultrahydrogel linear column with Waters differential refractometer detector. The column was calibrated for molecular weight using Varian polyethylene oxide standards. The GPC traces were normalised to the same maximum detector output in order to facilitate comparisons. The weight average molecular weight (M_w) and number average molecular weight (M_n) were determined from the output data. M_n, M_w and polydispersity (PD) are defined as:

$$M_n = \frac{\sum M_i N_i}{\sum N_i} \quad M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} \quad \mathrm{PD} = \frac{M_w}{M_n}$$

where N_i is the number of moles of each polymer species and M_i is the molar mass of that species.

In order to determine whether any degradation of the depressant molecule occurred during freeze drying, the chromatogram of the freeze dried reference samples were compared to depressant samples that had not been through the freeze drying process. This confirmed that the freeze drying did not alter the depressant molecular weight distribution in any way.

2.5. Adsorption isotherms

Talc was pulverised to 100% passing 38 μm. Approximately 0.5 g talc was weighed exactly into 250 mL conical flasks. 100 mL of the required depressant solution, made up in 1×10^{-2} mol/L, ionic strength $Ca(NO_3)_2{\cdot}4H_2O$ at pH9, was added to the talc. The flasks were covered and stirred in a constant temperature shaker bath at 25 °C for 24 h. Thereafter, samples were centrifuged at 5000 rpm for 10 min and 1 mL aliquots removed for analysis by the colourimetric Du Bois method (Du Bois et al., 1956). These were read against previously constructed calibration curves, specific to each depressant. The data was fitted to a Langmuir adsorption isotherm of the form

$$I_{ads} = I_{max}\left(\frac{KC_{eq}}{1 + KC_{eq}}\right) \tag{1}$$

where I_{ads} is the adsorption density, I_{max} is the maximum adsorption density, K is the Langmuir equilibrium constant and C_{eq} is the equilibrium depressant concentration.