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Effect of Ionic Surfactants on Bauxite Residues Suspensions Viscosity

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Abstract:

Measurement of the rheological property of bauxite residue sample received from an Australian alumina refinery, treated with a number of cationic and anionic surfactant in laboratory has been carried out using a Brookfield viscometer for the assessment of the effect of surfactants on the residue viscosity. It was found that sodium laurate, prepared with an excess of sodium hydroxide was found to be effective while direct addition of anionic surfactants (lauric acid and sodium laureth sulphate) and cationic (cetyl trimethyl ammonium bromide) produce only moderate effect on the red mud suspension apparent viscosity at 65 °C. The experimental data appear to confirm the crucial role of the cation sodium in the process of adsorption of anionic surfactants on the flocculated red mud particles.

Keywords: Red Mud, Bauxite residues, Rheology, Surfactant, Viscosity reduction.

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1. Introduction

The Bayer process is widely used in the alumina refinery industry for the production of alumina from bauxite. This process generates residue known as red mud in large quantity. In a typical alumina refinery, bauxite is dissolved in sodium hydroxide solution under pressure and elevated temperature to extract the alumina minerals leaving behind caustic insoluble minerals including iron (hematite mainly), titanium oxides (anatase and rutile) and silica gangue minerals (Bayer sodalite containing sodium aluminium silicate which is formed during the digestion process). These insoluble compounds are named collectively as red mud residue.

The residue material is separated from the liquor (which contains dissolved alumina after the extraction process) in large settlers/clarifiers. After the residue is washed in counter-current decanters with hot condensate to recover the valuable caustic soda component, the mud is disposed. In some refineries, the residue is diluted with sea water in the plant before disposal, where part of the caustic soda component in the liquor is neutralised by salt ions such Ca^{++} , Mg^{+} . This reduces the pH of the mud from 12-13 to 9-10. This process is commonly known in the industry as the seawater neutralisation process and its product is called neutralised mud. At the present, there is no viable process developed for utilising the bauxite residue, consequently this large quantity of waste material is required to be disposed economically and safely to the environment.

The common method for residue disposal is pumping the material to large settling ponds where on-land waste disposal is permissible [1, 2]. Typical problems associated with red mud pumping are high energy requirement, rapid wear of pipelines (due to erosion caused by the presence of large abrasive sand particles in some refineries), large land area required and significant environmental impact (due to the alkaline conditions of the liquor disposed with red mud). The magnitude of these problems can be reduced if the waste material is disposed at higher solid concentration. However this is at the expense of higher pumping cost since the apparent viscosity of the mud increases significantly as the solid concentration increases [3, 4, 5]. There is obviously incentive to reduce the residue viscosity at relatively high solid concentrations, so that the pumping cost can be minimised.

In general, the rheological behaviour of concentrated mud residues is affected strongly not only by solids loading, particle morphology and particle size distribution, but also by particle interactions. These interactions are influenced by chemical factors such as the presence of flocculant/dispersant agents. The practice of adding flocculants during clarification and mud washing is already used widely in the industry to promote the settling of particles during the solids separation process. High molecular weight negatively charged anionic polyacrylates are commonly used for the flocculation of bauxite residue in clarifiers/settlers. For mud washing, a mixture of acrylate and non-ionic acrylamide is often used.

Most of the published literature on the rheology of flocculated residues is related to the behaviour of the material without surfactants [6-10] while very limited work exists on how this behaviour is affected by surfactants [12,16].

Residue suspensions, without surfactants, can be classified as non-settling homogenous slurries provided the large particles fraction in the solids is negligible. At concentrations below 10% by weight, it behaves like a Newtonian fluid with a constant viscosity which varies only with liquor concentration and temperature. Between solid concentrations of 10% and 25%, mud suspensions exhibit the characteristics of shear thinning i.e. viscosity decreases with increasing rate of shear [2].

Capillary viscometry has been used to determine the relationship between shear stress and shear rate and the power law model is generally found suitable to describe the rheological behaviour of the suspension at low to medium solid concentrations [1, 11].

At higher concentrations, the suspensions become thixotropic and exhibit a yield stress in addition to the shear thinning behaviour [7]. The thixotropic behaviour means that the flow properties of the material are not only dependent on shear rate but also on time of shear and previous shear history. A vane-shear instrument was used [8] to measure the yield stress which defines the minimum shear stress that must be exceeded to start flow.

Hiroshue et al. [12] have conducted study of the effect of pH and surfactants on the dispersion of residue suspensions. They found that pH can influence the coagulation and dispersion of the suspension. Some extent of dispersion has been observed by the authors in the pH range of 8-11 at pH = 5. Complete dispersion of the suspension, however can only be obtained using surfactant sodium hexametaphosphate (which is also known as sodium polyphosphate). The optimum concentration of the surfactant was found to be between 0.1 and 1% by weight.

Hashimoto et al. [16] have investigated the dispersion of mud residue in non-aqueous media and found that linseed oil is effective to disperse the material in hexane and cyclohexane solutions.

Mechanism of the adsorption of anionic polymer flocculant on red mud particles and synthetic hematite has been proposed.

In their study of red mud flocculation using anionic polyacrylates, Chvedov et al [18] measured the surface charges of red mud particles generated from the laboratory digestion of various bauxites including Weipa bauxite. Using the method of potentiometric titration, it was found that the particles carry a significant negative charge under the basic condition. As polyacrylate is also anionic, it was speculated

that the adsorption of the polymer is possible with the presence of counter cation (such as sodium) which acts as an intermediate species in the process of flocculation. Fawell et al [15] examined the adsorption of polyacrylates on synthetic hematite using FTIR – ATR (Attenuated total internal reflectance). They found evidence of the polymer adsorption on the hematite particle under basic condition but only if there is enough counter cation (e.g. sodium) present in the solution. This essentially agrees with the results given in [18] above.

The above studies indicate the crucial role played by cations in the process of flocculant polymer adsorption on red mud particles and/or synthetic hematite particles.

Currently, at the School of Physical and Chemical Sciences (QUT) we are conducting a study of the rheological properties of bauxite residues from a number of Australian refineries with particular focus on the use of surfactants to reduce its viscosity. In the previous publication [19] we have established that sodium laurate solution, prepared with an excess in sodium hydroxide, is an effective surfactant for bauxite residues from an Australian refinery (Comalco Alumina Refinery in Gladstone, Queensland, Australia). In this short note, we will present additional results on the sodium laurate surfactant (i.e. the effect of cation sodium excess quantity) and the suitability of other types of anionic and cationic surfactants for the Comalco red mud residue will also be reported. Attempt will be made to explain the mechanism of the surfactant adsorption process using the laboratory data generated from this study.

2. Materials and methods

Red mud slurry from the last washer of the mud washing train (its solid concentration is approximately 540 g/L) was received from Comalco Alumina Refinery (Gladstone, Queensland, Australia)

The sample was stored in screw top containers. The red mud pH was found to be approximately 12.

The sample received was used directly and no attempt was made to alter the structure of the flocculated particles (e.g. stirring or adding more flocculant). For the preparation of suspensions at higher concentrations, the original mud was allowed to settle in containers and supernatant liquor was decanted. This supernatant liquor was kept for use in the preparation of samples of lower concentrations.

A Malvern size analyser (Mastersizer S model) was used to determine the sample particle size distribution. The results of the size distribution are shown in Table 1. The results are comparable to those for neutralised mud from QAL reported elsewhere [11].

Rheological measurements were carried out using a Brookfield rotational viscometer (Rheomat DVIII). All measurements of shear stress, shear rate and apparent viscosity were carried out in a temperature-controlled environment at 65°C to simulate typical plant conditions. The range of rotational speed was between 30 and 240 RPM corresponding to a shear rate range between 40 and 300 sec⁻¹. No quantification of the extent of particles settling was established during the course of measurement. However for the given particle size distribution (refer to Table 1) it is expected that settling would be minimum since the large particle size fraction in the red mud samples is negligible.

All measurement of the samples rheology with and without surfactants was carried at solid concentrations in the range of 500 g/L at 65 °C.

Cationic surfactant (cetyl trimethyl ammonium bromide), anionic surfactant (sodium laurath sulphate) and both the sodium hydroxide and lauric acid used in the preparation of sodium laurate surfactant solution were manufactured by Ajax Chemicals Ltd.

Sodium laurate solution was prepared by reacting lauric acid with caustic soda NaOH at various molar ratio NaOH : lauric acid ranging from of 1:1 to 10:1.

All surfactants were added to residue suspensions at the dosage rates of 1 % wt of surfactant/dry mud. After the addition of surfactant, measurements of shear stress at various shear rates were conducted using the Brookfield viscometer.

3. Results and discussion

3.1 Sodium laurate surfactant solution

In our previous work with red mud suspensions [19], we have found that sodium laurate surfactant solution, prepared at the NaOH: lauric acid molar ratio of 10:1, was effective for the reduction of the red mud suspension viscosity. It was speculated that the sodium cation, present in excess in the surfactant solution, causes neutralisation of the red mud particles surface charge thus allowing the surfactant head group (refer to Figure 1) to be attached to the red mud particles even though both are negative charged.

In this current work, additional results on the effect of varying the sodium excess level in the surfactant solution on the suspension viscosity are reported.

Figure 2 shows the influence of the molar ratio (ranging from 1:1 to 10:1) on the suspension apparent viscosity. As the ratio is increased, further reduction of the viscosity is observed until the ratio of 5:1 is reached; beyond this value no additional benefit was achieved.

The experimental data above seem to indicate that the role of the cation sodium in the process of the sodium laurate surfactant adsorption on the flocculated red mud particles may be similar to the role of the same cation in the process of flocculation of red mud particles and hematite particles reported in [18] and [15]. At higher solution ionic strength (i.e. higher in cation concentration) the extent of adsorption increased up to a certain level until the monolayer adsorption (of the surfactant molecule in this case) is completed.

It appears that the mechanism postulated for the adsorption of polyacrylate polymer on the red mud and synthetic hematite particles may be applicable for the sodium laurate-red mud particles system. This mechanism proposes that the adsorption on the negatively charged flocculated red mud particles (due to hematite and silicate bearing compounds) by an anionic surfactant such as sodium laurate can only possible with the presence of a cation (such as sodium).

For red mud particles generated from other types of bauxite (e.g. low in reactive silica), it is expected that the above model may still valid however the extent of cation sodium requirement may be different due to a lesser concentration of sodium

aluminium silicate compounds present in these red mud. This will need to be confirmed experimentally.

It is interesting to observe the positive effect of the sodium laurate surfactant was not observed with neutralised mud suspension as attempt to reduce the viscosity of neutralised mud suspension using similar sodium laurate surfactant solution have not achieved the same results as for the red mud suspension. It is speculated that the seawater neutralisation process at the plant may have caused alteration in the particles surface charges or in the chemical composition of the red mud (e.g. the composition of the silicate bearing compounds may be effected by the process) which in turn causes alteration to the surface charges. This aspect will need further work.

For a practical process involving the addition of the sodium laurate surfactant solution to bauxite residue, the beneficial effect (viscosity reduction) will need to be evaluated against a number of negatives aspects associated with the method. These include:

- (i) Additional cost of raw caustic (for the surfactant formulation)
- (ii) Impact (if any) of the excess caustic hydroxide to the pH of the red mud disposed to the environment.
- (iii) For refineries equipped with a neutralisation process downstream, the increased level of caustic soda in the red mud may also influence the neutralisation conditions (e.g. the quantity of seawater for neutralisation). This optimisation exercise is outside the scope of this work.

3.2 Anionic surfactants

Two anionic surfactants (lauric acid and sodium laureth sulphate) were tested for their effect on the red mud suspension viscosity. For process simplicity, these solid surfactants were added directly to the suspension without any additional preparation. Figure 3 compares the suspension apparent viscosity with and without the solids surfactant. A moderate reduction was observed (poorer than the sodium laurate surfactant reported in section 3.1 above), thus confirming some degree of dispersion was present albeit of limited extent.

The limited dispersion achieved with the direct addition method (of either surfactant) may be explained using the adsorption mechanism model postulated in 3.1 above. With lauric acid, it is possible that the residual free sodium hydroxide in the weak Bayer liquor (with the red mud residue) would react with the acid thus producing the surfactant head group. As the cation sodium is still present under the experimental conditions used in this work, the head group would still be able to attach to the red mud particles causing some degree of particles dispersion. Again it was found that neutralised mud when treated with direct addition of lauric acid has not shown significant reduction in the viscosity.

The benefit of this direct addition method of anionic surfactant to the red mud suspension is associated with its process simplicity; this requires no additional cost of raw caustic and a lesser environmental impact is possible. Once again, the suitability of the method -against a more effective dispersant such as the sodium laurate surfactant solution- would need to be evaluated with due consideration to the capital/operating cost and its environmental impact.

3.3 Cationic surfactant

Solid cationic surfactant, cetyl ammonium bromide, added directly to red mud suspension, was evaluated for its effect on the red mud viscosity. This is shown on Figure 4. It can be seen that the effect is only moderate and its effectiveness is comparable to that produced by the solid anionic lauric acid surfactant reported in 3.2 above. With the cationic surfactant addition, it is postulated that the negative charge on the flocculated red mud particle allows the cationic surfactant to be attached via the electrostatic forces. The limited success of the cationic surfactant may be associated with its limited dispersion ability.

4. Conclusions

The laboratory measurement of the red mud suspension viscosity in this work shows that sodium laurate solution (prepared with excess in sodium ion) is an effective dispersing agent for red mud. The maximum effectiveness is reached when the molar ratio is at 5:1.

For the case of direct addition of anionic surfactant (lauric acid and sodium laureth sulphate) and cationic surfactant (cetyl ammonium bromide), only moderate reduction in the red mud suspension viscosity was observed in all cases.

A mechanism for the adsorption of the anionic surfactants on the flocculated red mud particles was postulated using a model proposed for the adsorption of anionic polyacrylate polymer on red mud particles. The experimental results from this work appear to confirm the crucial role of the cation sodium in the surfactant adsorption process.

5. Acknowledgements

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References

1. Colombera, P.M. and Want, F.M., 1982. Chem. Eng. Aust. **7**, pp 36-40
2. Nguyen, Q.D. and Boger, D.V., 1987, Bauxite Tailings 'Red Mud', Wagh, A.S., Desai, P. (Eds), The Jamaica Bauxite Institute, pp 53-65,
3. Chandler, J.L., 1987, Bauxite Tailings 'Red Mud', Wagh, A.S., Desai, P. (Eds), The Jamaica Bauxite Institute, pp 101-105,
4. Cooling, D.J. and Glenister, D.J., 1992, Light Metal **1**, pp 25-31
5. Nguyen, Q.D. and Boger, D.V., 1998, Int. Journal of Min. Processing. Vol 54, pp 217-233
6. Nguyen, Q.D. and Boger, D.V., 1983. J. Rheol. **27**, pp 321-349
7. Nguyen, Q.D. and Boger, D.V., 1985. Rheol. Acta, **24**, p 427
8. Nguyen, Q.D. and Boger, D.V., 1985, J. Rheol. **29**, pp 335-347.
9. Green, M.D., de Guilhend. N.J., Nguyen, Q.D., Boger, D.V., 1992, Proc. Int. Bauxite Residue Workshop, Perth, Western Australia, pp 116-125
10. Pashias, N., Boger, D.V., Summers, J., and Glenister, D.J., 1996, Proc. 4th Int. Alumina Quality Workshop, Darwin, pp 507-515,
11. Samiento, G., Crabble, P.G., Boger, D.V., and Uhlerr, P.H.T., 1979, I. and E.C. Proc. Des and Dev., **18**, p 746.
12. Hiroshue, H., Abe, E., Yamaha, N., and Ihara, J., 1980, J. Powder Tech., **27**, p197,
13. Papo, A., Piani, L., and Ricceri, TR., 2002, Colloids and Surfaces A: Phys. and Eng. Aspects, Vol 201, pp 219-230.
14. Birdi, K.S., 1997, Handbook of Surface and Colloid Chemistry, CRC Press,
15. Fawell, P.D., Kirvan, L.J., and van Bronswijk, W., 2002. Proc. 6th Int. Alumina Quality Workshop, Brisbane, pp 301-308.
16. Hashimoto, T., Tobayama, M., 1982, Shokugyo Kunren Coll., vol 17, pp 204-208.
17. Jamieson, E., Cooling, D. J., Fu, J., 2005, Proc. 7th Int. Alumina Quality Workshop, Perth, pp 210-213.

18. Chvedov, D., Ostap, O., Le, T., 2001, Colloids and Surfaces A: Phys and Eng. Aspects, Vol 182, pp 131-141
19. Pejcinovic, N., Nguyen, T., Frost, R., 2006, Colloids and Surfaces A: Phys and Eng. Aspects (in print)

List of Figures

Figure 1: Proposed adsorption mechanism of Sodium Laurate onto RM surface

Figure 2: Effect of sodium laurate on red mud viscosity

Figure 3: Effect of direct addition of anionic surfactant on red mud viscosity

Figure 4: Effect of direct addition of cationic surfactant on red mud viscosity

List of Tables

Table 1: Particle size distribution of Comalco red mud and neutralised mud

Tables

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Particle size distribution	Micron
D ₁₀	13
D ₅₀	2.9
D ₈₀	6.5

Figures

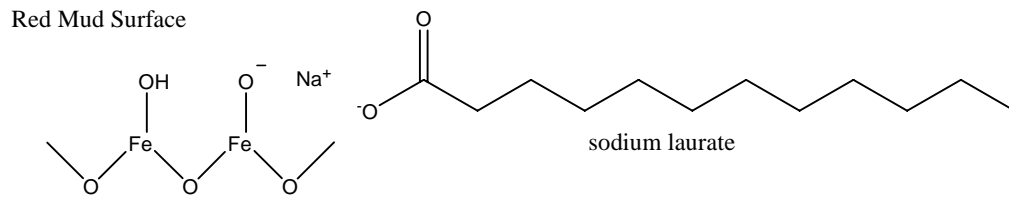


Figure 1: Proposed adsorption mechanism of Sodium Laurate onto RM surface

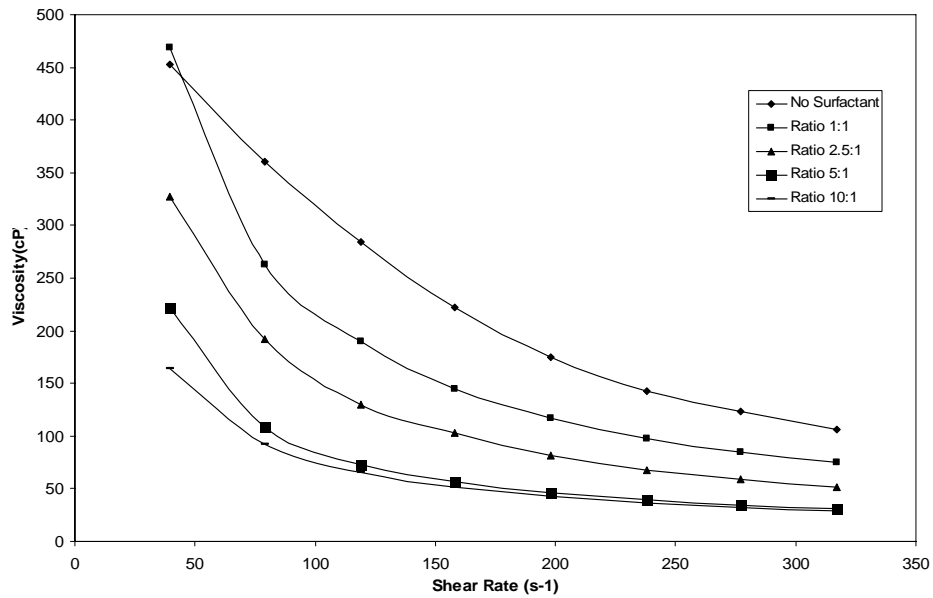


Figure 2: Effect of Sodium laurate on red mud viscosity

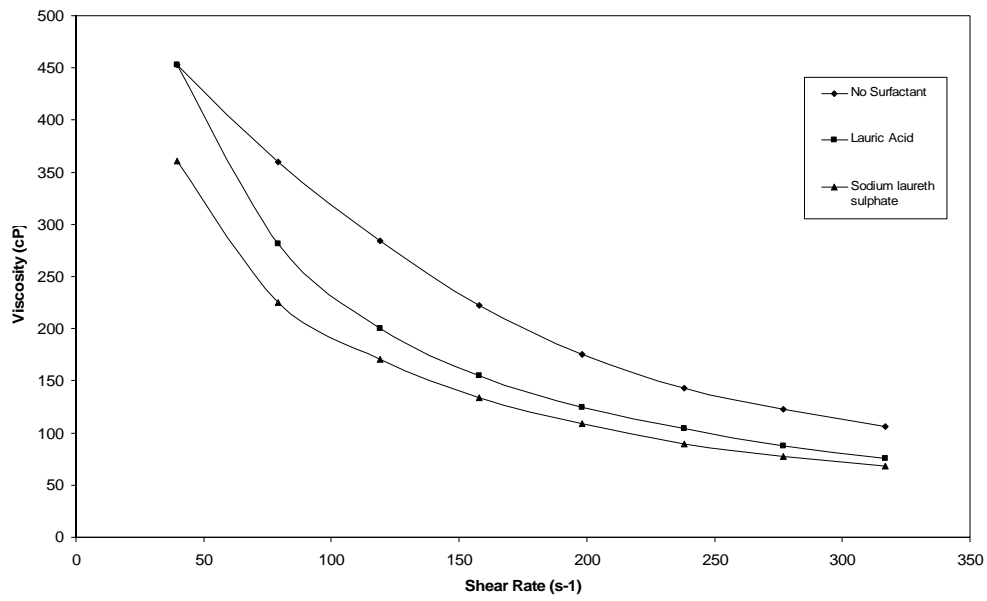


Figure 3: Effect of direct addition of anionic surfactants on red mud viscosity

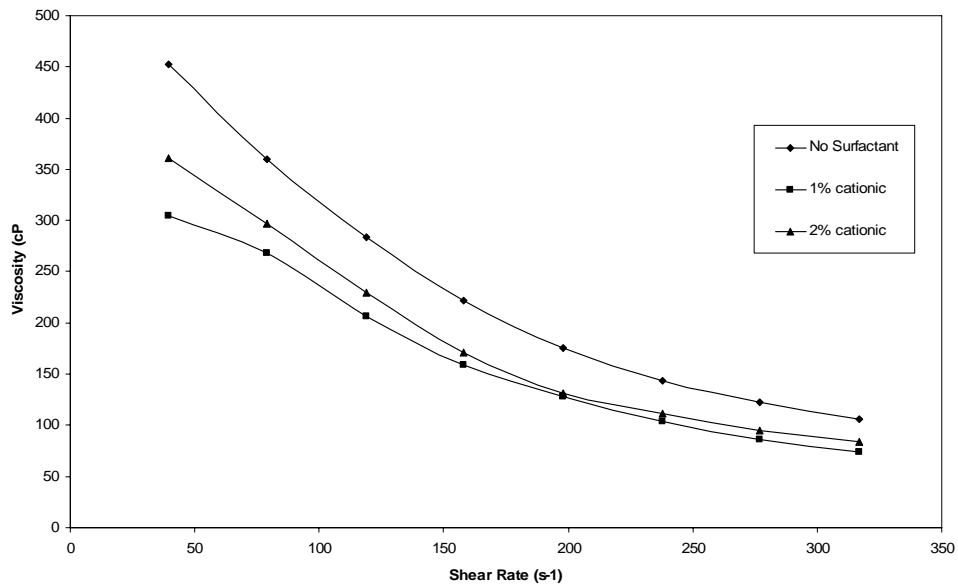


Figure 4: Effect of direct addition of cationic surfactant on red mud viscosity

