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# EFFECTS OF TEMPERATURE AND METHOD OF SOLUTION PREPARATION ON THE PERFORMANCE OF A TYPICAL RED MUD FLOCCULENT

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## Abstract

Alcan International Ltd. in collaboration with Ondeo Nalco Company have carried out a fundamental study on the dissolution and performance of a 100% anionic polymer. The effects of method of preparation, solvent composition, temperature and exposure time on flocculent activity under conditions relevant to both atmospheric and pressure decantation were investigated. Flocculent activity was determined using static and dynamic settling tests, and the results were correlated with the reduced specific viscosity (RSV). For any given method of preparation of the flocculent solutions (makeup/dilution) the RSV tended to decrease with increasing solution ionic strength, independent of ionic speciation. While a significant loss in flocculent activity occurred with long exposure of the solution to high temperature, only a minor loss occurred in the short time required to flocculate and settle the mud in a decanter operating at 150 °C. Recent results in an actual plant pressure decanter appear to validate this conclusion.

## Introduction

The aggregation of dispersed fine solid particles under the influence of a high molecular weight water-soluble polymer is thought to occur by the mechanism of bridging flocculation. Effective flocculation requires unoccupied sites on the particle surface for the adsorption of part of the polymer and that the adsorbed polymer extends into the liquid to allow adsorption onto other particles [1]. This implies that the polymer chain must be of sufficient size to bridge two or more particles together so that a network of bound particles (floccules) will form. In aqueous solution these polymers exist as intertwined randomly-coiled chains [2], and the equilibrium hydrodynamic volume (and radius of gyration) of these coils depend on the polymer molecular weight and structure, polymer charge density, polymer concentration and solution ionic strength [3, 4]. The electrostatic repulsion among the charged groups on the polymer provides the main driving force for the disentanglement of the polymer coils and, given enough time and sufficient dilution, the formation of individual extended polymer chains. A concentration of ions effectively shields the charged groups resulting in a smaller hydrodynamic volume. Thus, the influence of ionic strength is particularly important and its effect on the conformation of the polymer in solution is commonly determined by measuring the reduced specific viscosity (RSV), where a large RSV indicates a large hydrodynamic volume[3, 5].

In alumina refineries, solutions of flocculents used for the settling of red mud are prepared at various polymer concentrations and in a wide range of liquids, ranging from water to process liquor having high ionic strength. In addition, these solutions are exposed to different temperatures for varying periods of time before they are further diluted (secondary dilution) and applied to the decanters or washers. Secondary dilution is often done with a different liquid from that used for the preparation of the initial solution, further increasing the number of combinations of factors. Furthermore, the advent of high pressure decanters, used in the Alcan double digestion process, requires that the flocculents perform well at temperatures of 150 °C or greater [6]. Polyacrylate polymers, similar to those used as red mud flocculent, were shown to be stable up to 300 °C in high pH solutions [7]. However, previous work conducted at Alcan International Ltd. indicated a large loss in viscosity when solutions of polyacrylate were exposed to 150 °C for relatively short times. This observation provided the motive for a full investigation into the effects of method of preparation of flocculent solutions on performance as well as on their thermal stability. Since the ability of the polymer to engage in bridging flocculation depends on the hydrodynamic volume of the polymer in solution, the relation between settling performance and RSV was investigated. This study was meant to increase our understanding of the factors that contribute to flocculent activity and to apply this knowledge to maximize performance in the alumina refinery.

## Experimental

### General Method for Preparation of Polymer Solutions

All work was performed using the Ondeo Nalco red mud flocculent, N85110™, a latex product containing a homopolymer of acrylic acid. Using a cage mixer (30 minutes at ~600 rpm) initial dissolution (primary dilution) of N85110 was done by adding a specified weight of the neat N85110 into the required weight of makeup solvent to give N85110 concentrations ranging from 0.08 to 1.5%, by weight, as product. These were then diluted, when necessary, to give secondary dilutions containing 0.08% N85110, unless otherwise specified. The "solvents" used for the primary and secondary dilutions were aqueous solutions containing various combinations of NaOH, $Na_2CO_3$ and $NaAl(OH)_4$, or spent liquor taken from the Jonquière plant. In some cases deionized water was used for the secondary dilution. Heat treatment of the polymer solutions was performed, as described below, on either the primary or secondary dilutions.

### Method for Thermal Treatment of Polymer Solutions

In a few instances thermal degradation studies were performed at 60 °C, accomplished by simply holding the polymer solution in a sealed flask immersed in a water bath. In most cases, however, higher temperatures were used, necessitating a special apparatus that allows rapid heating to temperatures above the boiling point of the polymer solution. A coil (4 turns) was constructed from 175 mm of 6.4-mm stainless steel tubing and fitted with a Swagelock valve (No. SS4P4T) at each end. The internal volume of the coil was 25 $cm^3$.

The polymer solution (25 $cm^3$) was injected into the coil using a syringe. The valves were closed and the coil was immersed in a 1500-$cm^3$ stainless steel beaker containing oil (Dow Corning No. 710, flash point of 302 °C) preheated to the desired temperature. The oil was agitated with a magnetic stir bar over a hot plate, and the temperature was controlled by a thermocouple immersed in the oil. In most experiments the contact time at the elevated temperature was 30 minutes, but for some runs a contact time of just 2 minutes was used. Thermal equilibrium with the oil was reached in about 1 minute, so that a contact time of 2 minutes translates to an actual time of around one minute at the desired temperature.

Determination of Reduced Specific Viscosity (RSV)

Viscosity measurements on all flocculent solutions and solvents were made at 25.0 °C using an Ubbelholde tube, and averages of two or more measurements were recorded. All determinations were done at the same N85110 concentration of 0.080%. The reduced specific viscosity (RSV) was computed according to equation 1.

$$\text{RSV} = \frac{\left(\dfrac{\text{sample elution time}}{\text{solvent elution time}} - 1\right)}{\text{polymer concentration}} \qquad (1$$

Jar Tests for Red Mud Settling

Laboratory settling tests were performed in cylinders (jars) according to the Alcan standard procedure 1234-90 for testing red mud flocculents. This method makes use of 1000-$cm^3$ graduated cylinders immersed in a controlled temperature bath set to 95 °C to simulate liquor decanter conditions. The cylinders were equipped with a rake to cut channels in the mud bed and improve the mud compaction. All settling tests were conducted using settler feed slurry from Alcan, Jonquière, Quebec.

The slurry in the cylinder was mixed by plunging with a rubber stopper affixed to a metal rod, and the desired amount of flocculent was added and uniformly dispersed using the plunger. The settling rates were calculated by recording the position of the interface as a function of time. Overflow clarity was determined by filtering a portion of the supernatant liquor through a 0.45µm Millipore filter one hour following the start of the settling test. The concentration of the consolidated solids was determined gravimetrically after two hours of raking according to the standard procedure.

Dynamic Red Mud Settling Procedure (C-FLOC™)

Dynamic red mud settling tests were done using the Alcan Settling Analyzer, C-FLOC [8]. This instrument consists of a Plexiglas column (0.85 m long) equipped with a feed well at the top and a raking mechanism at the bottom. An external water jacket maintains the column at the desired constant temperature. A variable speed pump continuously feeds the solids slurry of known concentration at the top of the feed well. Synthetic flocculent solution can be added at one or two injection points into the slurry feed line. The dosage was set to the minimum required to give good flocculation and maintain steady-state decantation (constant slurry feed rate, mud underflow rate, supernatant clarity and mud/liquor interface level). All settling tests were conducted using settler feed slurry from Alcan, Jonquiѐre, Quebec.

The overflow liquor was collected at the top of the column for the determination of clarity (suspended solids). To get a good estimate of the clarity compared to actual plant data, the collected overflow sample was kept undisturbed in a water bath at 95°C for 60 minutes. This period of time was required to simulate the liquor residence time in a plant decanter. After this time, a portion of the sample was removed and filtered under vacuum to obtain the amount of total suspended solids

The thickened underflow solid was withdrawn at the rate needed to maintain the bed height of the solids (interface level) constant in the test column. The slurry feed rate was set between 150 and 250 $cm^3$/min. to allow good reaction time in the column and to avoid settling of solids in the slurry feed line. In these experiments the effective liquid rise velocity ranged from 3 to 7.5 m/h.

## Results and Discussion

Effects of Solvent and Method of Preparation on Polymer RSV

The effects of caustic soda (CS), total titratable soda (TTS) and alumina on the RSV of dilute flocculent solutions was investigated using four different solvents, listed in Table I. For each solvent three methods of preparation (Table II) were used such that the final composition obtained with each method was constant with respect to CS, TTS and alumina content (though each solvent produced a different final composition). Thus, 12 polymer solutions, all containing 0.08 wt% N85110, were prepared. The effects of solvent composition and method of preparation was assessed from RSV measurements.

Table I Solvents Used for the Preparation of 0.08 wt% N85110

| Solvent | Type | Composition | | |
|---|---|---|---|---|
| | | CS[1] | TTS[1] | $Al_2O_3$[2] |
| S1 | spent liquor | 16.6 | 19.8 | 6.3 |
| S2 | NaOH | 16.6 | 16.6 | 0 |
| S3 | NaOH, $Na_2CO_3$ | 16.6 | 19.8 | 0 |
| S4 | NaOH, $Na_2CO_3$,$Al_2O_3$ | 16.6 | 19.8 | 6.3 |

[1] As wt% $Na_2CO_3$ [2] As wt% $Al_2O_3$

Table II Methods for Preparation of N85110 Solutions

| Method | Primary Dilution | Secondary Dilution |
|---|---|---|
| A | To 1.5% in aqueous NaOH. | To 0.08% in solvent and water. |
| B | To 1.5% in solvent. | To 0.08% in solvent and water. |
| C | Directly to 0.08% in solvent and water. | |

As shown in Figure 1 the RSV of N85110 in dilute solutions was affected by both the solvent and the method of preparation. For all solvents the RSV decreased as the TTS in the primary dilution was increased even though the composition of the secondary dilutions, on which the RSV measurements were made, was held constant. Thus, dilution Method A always gave the highest RSV while Method B gave the lowest. The presence of the carbonate ion appeared to have no effect, since S2 and S3 produced nearly identical results. However, the aluminate ion exerted a negative effect, but mainly when the flocculent was inverted in the neat solvent (Method B). For each dilution method spent liquor (S1) always gave the lowest RSV, indicating that some component in the plant liquor (other than carbonate and aluminate) was interfering with the dissolution of the polymer.

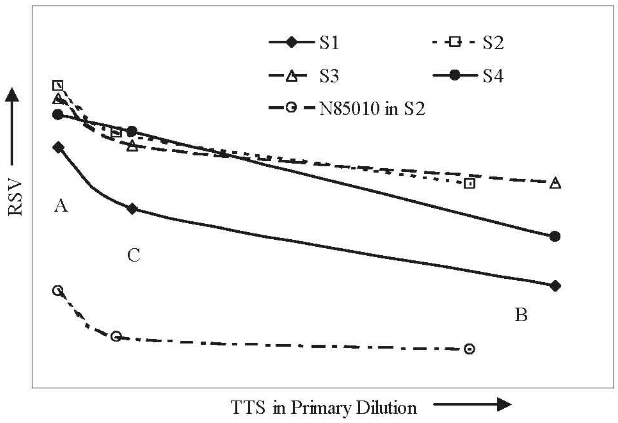


Figure 1: Effects of Solvent and Method of Dilution on RSV of N85110 and N85010.

All dilute N85110 solutions formed a small amount of low-density white precipitate after standing undisturbed for 24 hours. The worst cases occurred for flocculent diluted directly into highly caustic solutions (Method B). Analysis of the precipitate by infrared spectroscopy indicated the presence of hydrocarbon oil and ionic surfactants, both of which are contained in the N85110 emulsion. There was no evidence of polymer in this solid, hence the shape of the curves in Figure 1 was not due to precipitation of the polymer. This was supported by the result obtained using a powder flocculent, N85010™, where the curve is almost parallel with that for N85110 prepared in the same solvent system. The RSV for solutions of N85010 was lower due the smaller intrinsic hydrodynamic volume (smaller molecular weight and/or more cross linking of the polymer chain) of the powder flocculent. As expected, the dry flocculent did not form any precipitate since neither hydrocarbon oil nor ionic surfactant are present in this product.

Clearly, both the solvent and method of preparation affected the RSV. The nature of these effects was further explored in experiments where controlled amounts of $NaNO_3$ and NaCl were added to a solvent very similar to S4. The flocculent solutions were prepared according to Method A. These results are presented in Figure 2. Thus, the hydrodynamic volume, as assessed by RSV, depended only on the total sodium ion concentration. While the effects of nitrate and chloride ions were negligible, it is possible that other anionic species in Bayer liquor have a direct or indirect influence, as mentioned above for the aluminate ion.

The data displayed in Figure 2 cover a small TTS range, and the relationship appears linear over this domain. But, over a much wider range the RSV varied exponentially with TTS, as shown in Figure 3. This exponential relationship fit the data remarkably well especially considering that the data were taken from 0.08% N85110 solutions prepared in a variety of solvents and using different methods of preparation.

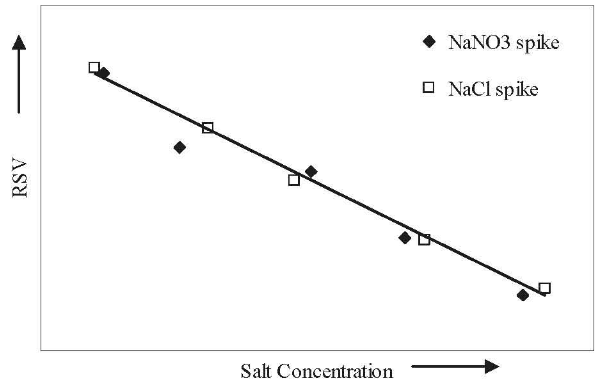


Figure 2: Effect of Salt Concentration on the RSV of Dilute N85110 Solutions.

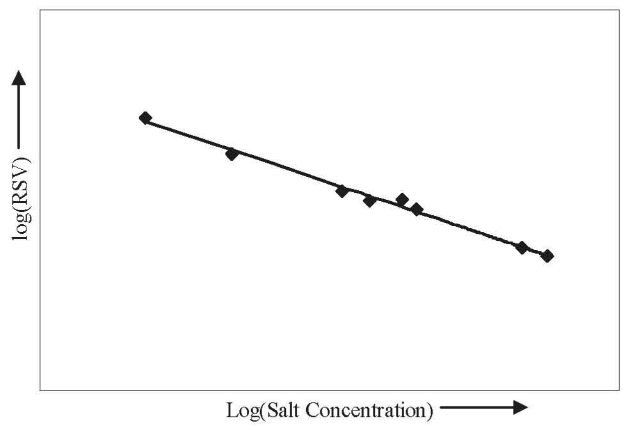


Figure 3: Effect of Salt Concentration on the RSV of Dilute N85110 Solutions.

<u>Thermal and Solvent Effects on RSV and Red Mud Settling Performance of N85110 Made up in NaOH Solutions</u>

Thus far only the effects of solvent and method of preparation of N85110 solutions upon polymer confirmation, as related to RSV, was investigated. In this section the effects of exposure of the flocculent solutions to various temperatures, in combination with the influence of solvent and method of polymer dissolution, are presented. The temperatures for this investigation were chosen to assess the amount of degradation expected during the storage of polymer solutions and on the loss in activity occurring while the polymer is in contact with the mud in conventional and in high temperature decanters.

The effects of flocculent concentration, NaOH concentration, temperature and time of exposure were tested using a full factorial design (16 experiments). The range of each factor is listed in Table III. Thus, N85110 solutions were prepared in aqueous NaOH (primary dilutions) and exposed to the required temperature for different times. Following heat treatment the flocculent solutions were diluted (secondary dilution) using combinations of water and 200 g/l NaOH solution to produce sixteen polymer samples containing 0.08% N85110 and 40 g/l TTS. These final solutions were used for the determination of RSV and for running static settling tests (jar tests) on red mud slurry. The settling tests were conducted using a constant flocculent dose.

Table III Factors for N9779 Made up in NaOH Solutions

| Factors | Low | High | Units of Measure |
|---|---|---|---|
| Floc. Dose | 0.2 | 1 | Weight % |
| NaOH Conc. | 0.5 | 10 | Weight % $Na_2CO_3$ |
| Exposure Temp. | 60 | 150 | C° |
| Exposure Time | 2 | 30 | minutes |

The data were fitted with a mathematical model (correlation coefficient of 0.963) that relates the effects of the four factors on RSV. The behavior of this model can be represented by the effects cube diagram shown in Figure 4. Examination of this figure shows that:

1. RSV was not affected by exposure to low temperature. So, it is likely that plant ambient temperatures as high as 60 °C are not sufficient to cause significant RSV degradation if the flocculent is prepared under ideal conditions.

2. At high temperature, longer exposure time resulted in RSV degradation. But, in an actual plant exposure to the extreme temperature would only occur for a very short time before the flocculent interacts with the suspended solids to form stable aggregates.

3. Under all conditions of temperature and exposure time higher TTS gave lower RSV, consistent with the data presented above. This has obvious implications for the preparation of flocculent solutions having the best possible activity in the plant environment.

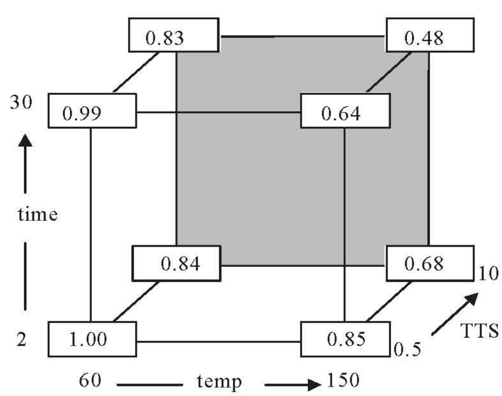


Figure 4: Effects of Temperature, Time and TTS on the Relative RSV of N85110, (shown in the boxes).

It is expected that formation of aggregates by the mechanism of bridging flocculation should be favored by a large hydrodynamic volume of the flocculent polymer in solution. If the RSV may be taken as an indication of hydrodynamic volume, then the settling rate should increase with increasing RSV, as demonstrated in Figure 5. These results suggest that for a given flocculent the RSV uniquely determine the settling performance, regardless of how the flocculent was prepared. As will be shown subsequently, this is not necessarily true when the flocculent is made up in plant liquor.

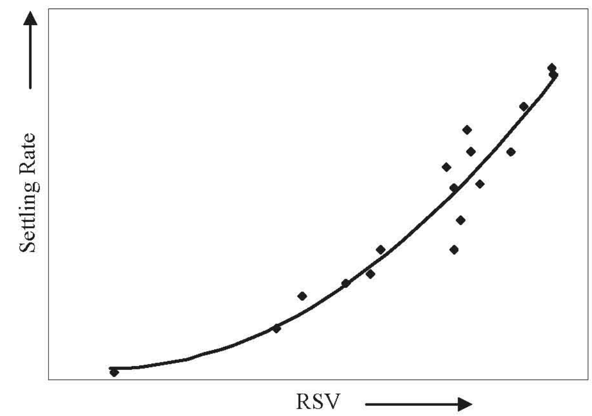


Figure 5: Effect of RSV on the Settling Performance of N85110.

Thermal and Solvent Effects on RSV and Red Mud Settling Performance of N85110 Made up in NaOH Solutions or in Spent Liquor

Flocculent solutions in plants are generally prepared at 0.15 – 0.6 wt% (on polymer actives basis) by dissolving the flocculent emulsion or powder in aqueous NaOH containing between 10 and 40 g/l TTS. The concentrated stock solution is often stored in the plant at a temperature of between 20 and 60 °C for periods ranging from 6 to 24 hours. This represents an ideal situation, and many plants perform the initial dissolution using some liquor stream that contains sodium aluminate and sodium carbonate. To cover the conditions encountered in the high temperature decanters, the thermal stability was examined at 150 °C, as well as at unusually long storage times.

Primary dilutions of N85110 (1.5%), prepared in aqueous NaOH at 10 and 40 TTS, were exposed to various temperatures for different periods of time. They were then diluted in DI water to 0.08% flocculent (secondary dilution) and the RSV and red mud settling rates were determined. The results are listed in Table IV.

Table IV Effects of Temperature and Holding Time on N85110 Solutions Made up to 1.5% in Aqueous NaOH, Heat Treated and Diluted to 0.08% in Aqueous NaOH

| Initial TTS (g/l) | Temp. (°C) | Time (min.) | Final TTS (g/l) | Relative RSV | Relative Settling Rate |
|---|---|---|---|---|---|
| 10 | 22 | 6 | 0.53 | 1.0 | 1.0 |
| 10 | 22 | 24 | 0.53 | 1.0 | |
| 10 | 22 | 30 | 0.53 | 1.0 | 2.1 |
| 10 | 22 | 78 | 0.53 | 1.0 | |
| 10 | 60 | 6 | 0.53 | 0.9 | 1.3 |
| 10 | 60 | 24 | 0.53 | 0.7 | 0.8 |
| 10 | 150 | 0.5 | 0.53 | 0.7 | 0.4 |
| 40 | 22 | 6 | 2.13 | 0.5 | 1.0 |
| 40 | 22 | 24 | 2.13 | 0.5 | |
| 40 | 22 | 24 | 2.13 | 0.5 | |
| 40 | 22 | 30 | 2.13 | 0.5 | 3.0 |
| 40 | 22 | 78 | 2.13 | 0.5 | |
| 40 | 60 | 6 | 2.13 | 0.5 | 2.0 |
| 40 | 60 | 24 | 2.13 | 0.5 | 1.5 |
| 40 | 150 | 0.5 | 2.13 | 0.4 | 0.8 |
| 0.53[1] | 150 | 0.5 | 0.53 | 0.6 | 0.4 |
| 2.13[1] | 150 | 0.5 | 2.13 | 0.3 | 0.5 |

[1] Made up directly at the indicated TTS, heat treated and tested without further dilution.

These results indicate that there was little degradation of RSV with the longer treatment time when the flocculent solutions were maintained at 22 or 60 °C. However, at 150 °C a significant loss in RSV occurred even with an exposure time of 0.5 hours. An even larger reduction in RSV was observed when the flocculent was made up directly to 0.08% and exposed to 150 °C. As expected, the 40 g/l TTS samples showed lower RSV than the 10 g/l TTS samples. The RSV appeared to follow a consistent trend with respect to TTS, temperature and exposure time. The settling rate showed a similar dependence, though the experimental error was larger in this case. The trend suggests that the settling rate was adversely affected only at the highest exposure temperature of 150 °C. However, it must be emphasized that flocculent solutions would not be exposed to this extreme temperature except in the decanter, where reaction with the mud occurs almost instantaneously and no reduction in performance is expected.

Some alumina refineries prepare primary flocculent solutions using spent liquor or some other stream containing a high level of caustic soda and alumina. Hence, the thermal stability of a 1.5% N85110 solution prepared in spent liquor containing 230 or 354 g/l TTS was investigated. As before, the primary dilutions were exposed to heat and then diluted to 0.08% flocculent using deionized water before determining the RSV and settling rate. Results are listed in Table V.

The RSV of the samples listed in Table V are lower than those presented in Table IV because the sodium ion concentration is higher. Notably, there was no appreciable loss in RSV even at the highest exposure temperature. Furthermore, within the experimental error inherent in the settling tests, there was no significant loss in performance for all the conditions tested. This suggests that the small hydrodynamic volume of the polymer in high ionic strength solutions tends to protect the flocculent against any structural or chemical degradation.

Table V Effects of Temperature and Holding Time on N85110 Solutions Made up to 1.5% in Spent Liquor, Heat Treated and Diluted to 0.08% in Deionized Water

| Initial TTS (g/l) | Temp. (°C) | Time (min.) | Final TTS (g/l) | Relative RSV | Relative Settling Rate |
|---|---|---|---|---|---|
| 230 | 22 | 0 | 10.2 | 1.0 | 1.0 |
| 230 | 22 | 24 h | 10.2 | 0.9 | |
| 230 | 22 | 72 h | 10.2 | 0.9 | |
| 230 | 22 | 0 | 10.2 | 1.0 | 1.1 |
| 230 | 105 | 2 | 10.2 | 1.0 | 0.5 |
| 230 | 105 | 30 | 10.2 | 1.0 | 0.7 |
| 230 | 150 | 2 | 10.2 | 0.9 | 0.9 |
| 230 | 150 | 30 | 10.2 | 0.9 | 0.9 |
| 354 | 22 | 0 | 14.9 | 0.9 | 1.0 |
| 354 | 22 | 24 h | 14.9 | 0.8 | |
| 354 | 22 | 72 h | 14.9 | 0.7 | |
| 354 | 22 | 0 | 14.9 | 0.9 | 1.1 |
| 354 | 105 | 2 | 14.9 | 0.8 | 0.8 |
| 354 | 105 | 30 | 14.9 | 0.8 | 0.9 |
| 354 | 150 | 2 | 14.9 | 0.8 | 0.8 |
| 354 | 150 | 30 | 14.9 | 0.8 | 0.7 |

An examination of all the data (Tables IV and V) suggests that the effect of RSV upon flocculent performance, as assessed by the settling rate, is strongly influenced by the ionic strength of the polymer solution, as demonstrated in Figure 6. The TTS within each set of data was held constant, but a different TTS was used for each set. So, it appears that RSV can be used as a predictor of settling rate only when the TTS of the final flocculent solution is held constant. This holds even if the primary dilution is made with varying conditions, with respect to TTS, exposure temperature and exposure time. Thus, very high RSV is not required for good settling, at least not in the TTS range reported here.

In summary, the total soda concentration (ionic strength) affects the RSV degradation of the flocculent. When the soda concentration is between 10 and 40 g/l TTS (typical for plant flocculent stock solutions) a significant degradation was observed only at the highest temperature tested (150 °C). The amount of degradation occurring between 60 and 150 °C should be investigated to determine the upper limit for temperature stability. In any case, stock solutions are generally kept well below 60 °C, and thermal degradation under these conditions is not expected to be significant. When high caustic soda concentrations are used for preparing the polymer no structural degradation occurs, but the higher soda level does reduce the RSV. At a constant TTS the settling rate increased with increasing RSV, but settling rates obtained with flocculent solutions having different ionic strength cannot be directly compared.

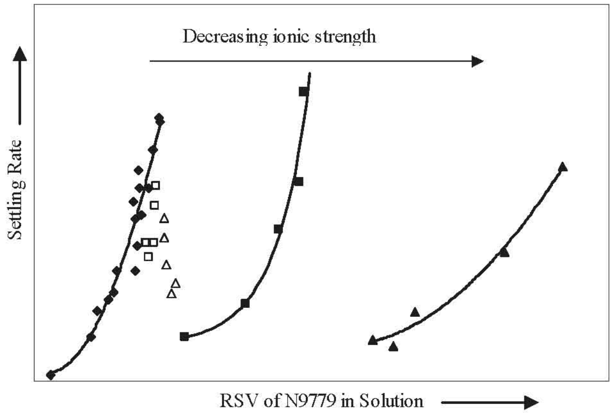


Figure 6: Effect of RSV on Settling Rate for N85110 Made up at Various TTS.

Thermal stability of 0.08% N85110 Made up in Aqueous NaOH and Diluted in Spent Liquor

Thus far, most of the solutions were prepared by initial dissolution of the flocculent in aqueous NaOH or refinery liquor, followed by secondary dilution in water. But, flocculents may also be introduced into the red mud decanters by injecting the primary flocculent solution directly into a circulating liquor stream. In this situation the flocculent may be exposed to high soda and high temperature in the dilute state before contacting the mud. Temperatures as high as 150 °C (high pressure decanters), TTS concentrations up to 340 g/l and exposure time as long as 2 minutes may be encountered. Thus, tests were conducted to determine the effects of total soda, temperature and exposure time of N85110 solutions made up in aqueous NaOH and diluted to 0.08% in spent liquor before thermal treatment. Hence, in this series of tests the thermal treatment was done on the fully diluted flocculents. The results are listed in Table VI.

Even at the highest temperature no RSV degradation was observed, suggesting that no loss in performance is expected. The low RSV observed here is a reflection of the high final TTS in the dilute flocculent solutions. So, any reduction in activity relative to the solutions presented in Tables IV and V is just due to the higher soda levels.

Table VI Effects of Temperature and Time on N85110 Solutions Made up to 1.5% in Aqueous NaOH and Diluted to 0.08% in Spent Liquor Before Heat Treatment

| Spent Liquor TTS (g/l) | Temp. (°C) | Time (min.) | Final TTS (g/l) | Relative RSV |
|---|---|---|---|---|
| 220 | 22 | 0 | 212 | 1.0 |
| 220 | 22 | 24 h | 212 | 0.9 |
| 220 | 105 | 30 | 212 | 0.9 |
| 220 | 105 | 30 | 212 | 0.9 |
| 212 | 22 | 0 | 337 | 0.9 |
| 212 | 22 | 2 | 337 | 0.9 |
| 212 | 105 | 30 | 337 | 0.9 |
| 212 | 105 | 30 | 337 | 0.8 |

Static and Dynamic Settling Tests on Thermally Degraded N85110 Solutions

Flocculent performance has been assessed by conducting static red mud settling tests, as well as measuring RSV. To further validate these results flocculent performance was also evaluated in dynamic settling tests using the Alcan Settling Analyzer, C-FLOC. Thus, tests were conducted on N85110 made up in aqueous NaOH, heat treated and then diluted in either aqueous NaOH or spent liquor. The results obtained using static and dynamic settling tests are listed in Tables VII and VIII, respectively.

Table VII RSV and Static Settling Tests for N85110 Made up to 1.5% in Aqueous NaOH (10 g/l TTS), Heat Treated and Diluted to 0.08% in Aqueous NaOH (10 g/l TTS)

| Temp, (°C) | Time (h) | Relative RSV | Relative Floc Dose | Settling Rate (m/h) |
|---|---|---|---|---|
| 22 | 2 | 1.0 | 1.0 | 6 |
| 22 | 2 | 1.0 | 2.1 | 52 |
| 60 | 24 | 0.9 | 1.1 | 10 |
| 60 | 24 | 0.9 | 2.1 | 34 |
| 150 | 0.5 | 0.6 | 2.0 | 7 |
| 150 | 0.5 | 0.6 | 4.1 | 27 |
| 22 | 0 | 2.0 | 1.3 | 32 |
| 150 | 0.5 | 1.1 | 1.3 | 3 |

[1]Diluted to 0.08% in deionized water following heat treatment.

Consistent with previous data, Table VII indicates that little loss in settling performance occurred when the flocculent solution was heated to 60 °C for 24 hours. Though a significant loss in activity was evident for the solutions heated to 150 °C, it is possible to recover settling performance by increasing the dose. As expected, both the RSV and the settling performance improved when secondary dilution was done in water, but the degradation suffered at 150 °C was just as severe.

Table VIII RSV and Dynamic Settling Tests for N85110 Made up to 1.5% in Aqueous NaOH (g/l TTS), Heat Treated and Diluted to 0.08% in Aqueous NaOH (g/l TTS)

| Temp, (°C) | Time (h) | Relative RSV | Rise Velocity (m/h) | Relative Floc Dose |
|---|---|---|---|---|
| 22 | 0 | 1.0[1] | 4.5 | 1.0 |
| 22 | 0 | 1.0[1] | 6.0 | 1.5 |
| 150 | 0.5 | 0.6[1] | 4.5 | 2.3 |
| 150 | 0.5 | 0.6[1] | 6.0 | 2.7 |
| 22 | 2 | 0.5 | 5.1 | 1.7 |
| 22 | 2 | 0.5 | 13 | 1.0 |
| 60 | 24 | 0.4 | 5.0 | 1.2 |
| 60 | 24 | 0.4 | 13 | 1.0 |
| 150 | 0.5 | 0.3 | 5.1 | 2.7 |

[1]Diluted to 0.08% in deionized water following heat treatment.

As evident in Table VIII, The required dose to settle the mud under steady-state dynamic settling conditions increased significantly when the flocculent solution was heated to 150 °C. It was necessary to increase the flocculent dose by 50 to 100% to maintain control of the settling, consistent with the loss in RSV. The flocculent dose used for the 22 °C sample settling at 5.1 m/h was anomalously high, and the cause for this is not known. In any case, the results shown in VII and VIII indicate that no significant loss in flocculent activity is expected to occur during the storage of 1.5% solutions even at temperatures at least as high as 60 °C.

To simulate conditions where flocculent is introduced into the red mud decanters by injecting a dilute solution into the blowoff slurry or into a solids-free liquor, N85110 was diluted in spent liquor prior to heat treatment. Table IX summarizes the results obtained with N85110 made up to 1.5% in aqueous NaOH (10 g/l TTS), diluted to 0.08% in spent liquor (260 g/l TTS) and exposed to various temperatures. The RSV results are presented together with the static settling tests and the flocculent dose required to settle the mud under dynamic conditions (C-FLOC). As indicated, two separate red mud samples were used for this test so that comparison between the two is tenuous.

Table IX RSV and Dynamic Settling Tests for N85110 Made up to 1.5% in Aqueous NaOH (10 g/l TTS), Heat Treated and Diluted to 0.08% in Spent Liquor (220 g/l TTS)

| Temp, (°C) | Time (h) | Relative RSV | Rise Velocity (m/h) | Relative Floc Dose |
|---|---|---|---|---|
| 22 | 0 | 1.0 | 4.5 | 1.0 |
| 22 | 0 | 1.0 | 6.0 | 1.0 |
| 150 | 0.5 | 0.9 | 4.5 | 1.1 |
| 150 | 0.5 | 0.9 | 6.0 | 1.9 |
| 22[1] | 24 | 1.0 | 5.1 | 2.5 |
| 22[1] | 24 | 1.0 | 13 | 1.8 |
| 60[1] | 24 | 1.1 | 4.9 | 3.0 |
| 60[1] | 24 | 1.1 | 13 | 3.5 |
| 150[1] | 0.5 | 1.2 | 5.1 | 3.2 |

[1] Different red mud sample

The RSV for all the tests listed in Table IX changed little, as was found for the flocculent samples made up in spent liquor (Table V). Again, the high ionic strength of these solutions ensures a small hydrodynamic volume that appears to protect the polymer from RSV degradation. It may also be that any change in the polymer conformation in solution is masked by the already small hydrodynamic volume at the high ionic strength. The required dose for constant settling was found to increase as the flocculent solutions were exposed to higher temperatures, in spite of the constant RSV. Thus, in this case RSV is not an accurate predictor of flocculent activity. Even so, the loss in activity is not large and can be overcome by increasing the flocculent dose. Degradation at 60 °C is slow and it is unlikely that flocculent solutions will be exposed to this temperature for periods as long as 24 hours. While the RSV and settling performance were lower when the flocculent was made up in high ionic strength solution, such as spent liquor, these solutions were thermally more robust. As noted previously, the loss in activity occurring at 150 °C does not necessary imply that this flocculent would be ineffective in a high pressure decanter. In fact, N85110 has been used successfully in the first commercial high pressure decanter operating at the Gramercy alumina refinery operated by Kaiser Aluminum Corporation (9).

## Conclusions

The RSV and settling performance of N85110 strongly depends on how the solution is prepared. The RSV decreases as the ionic strength of the solution increases, essentially independent of the type of ionic species. This is especially true during the primary dilution, even if the ionic strength following secondary dilution is held constant. The carbonate ion had no effect while aluminate appeared to cause a small reduction in RSV. For the same method of solution preparation the settling rate increases exponentially with RSV. But, different relationships between RSV and settling performance are obtained for different methods of solution preparation. Hence, RSV cannot be used as an absolute indication of settling performance.

The RSV and settling performance also depends on the thermal history of the flocculent solution. Little loss in RSV and settling performance occurs at temperatures up to 60 °C., and a significant loss occurs at 150 °C. However, relatively long exposure times are required and this condition is not likely to be found in most alumina refineries. The relative degradation in RSV and loss in settling performance are less when the flocculent is made up in high ionic strength liquor, but the overall performance is not as good as flocculent made up in low ionic strength solutions. The thermal stability is sufficiently high to allow the efficient use of N85110 in high pressure decanters.

Under ideal conditions primary dilutions of the latex flocculent, such as N85110, would be made at 1 – 1.5% in NaOH solution containing no more than 40 g/l TTS. This flocculent solution can be stored safely for at least 24 hours at temperatures not exceeding 60 °C. If plant liquor is to be used it is preferable to use the lowest TTS liquor possible. Secondary dilution should be done such that the final TTS does not exceed 40 g/l, using any stream free of soluble metals and containing no suspended solids. Of course, in actual application higher TTS liquors are favored to avoid liquor dilution. While plant liquors may be used, as is frequently the case, then the TTS should be kept to a minimum. These guidelines apply for applications in the high pressure as well as the convention decanters. While a small to moderate loss in activity can be expected for the high pressure decanters, this loss can be recovered by increasing the flocculent dose.

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