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The use of ultra-flocculation in optimization of the experimental flocculation procedures

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Abstract. The use of sea water in the flotation of Cu-Mo sulfide ores requires better understanding of the effect of electrolyte concentration on performance of flocculants used in the solid/liquid separation unit operations. This paper deals with optimisation of the experimental procedure that will be used in studying the effect of sea water on flocculation.

In the tests reported in this paper the tailings from one of Chile major flotation plants were subjected to the flocculation tests with Orifloc-2010 polyacrylamide in a Couette type reactor. It was shown that the flocculation efficiency can be dramatically improved by optimising the shear rate in the reactor, and that the procedure based on the ultra-flocculation can be used as a standardized experimental procedure in testing flocculants.

keywords: solid/liquid separation, flocculation, flocculants, flocculant testing, sedimentation

1. Introduction

The flocculants used by mineral processing industry are high molecular weight polymers that are soluble in water. Since a polymer can be soluble in water only if it is very hydrophilic these macromolecules must strongly interact with water and the properties/conformation of such macromolecules in water must depend on the polymers-solvent interactions. This is referred to as “goodness of solvent”.

The main function of polymeric flocculants is to produce large and strong flocs. It is generally accepted that polymers used as flocculants aggregate suspensions of fine particles by a bridging mechanism. The bridging is considered to be a consequence of the adsorption of the segments of the flocculant macromolecules onto the surfaces of more than one particle. As pointed out by Kitchener (1972), the merit of modern polymeric flocculants is their ability to produce larger, stronger flocs than those obtained by coagulation. Theoretically, the flocculants may be applied either after destabilizing of the suspension via coagulation, or without prior destabilization:

– stable suspension → coagulation → flocculant addition→ flocculation
– stable suspension → flocculant addition→ flocculation.

It is known that flocculants are not very effective for treating stable suspensions and so the first option, which involves prior destabilization by coagulation, is always better.

Hogg et al. (1993) showed that the appropriate choice of flocculants is determined primarily by chemical factors (mineral composition, solution chemistry, etc.), but the performance of the flocculant depends more on physical variables, such as agitation intensity and the rate of flocculant addition.

Several techniques have been proposed to determine the settling velocity in laboratory experiments, the "jar tests" being the most common (Coe and Clevenger 1916; Richardson and Zaki 1954; Michael and Bolgers 1962). Jar tests involves homogenizing suspensions in settling cylinders, introducing the flocculant and mixing by moving a plunger up and down in the cylinders, or by inverting the cylinders several times. This procedure is claimed not to be satisfactory because of the local over-dosing that can occur when the relatively concentrated flocculant solution meets the slurry (Kitchener 1978); but more important is that the agitation in this method does not produce the optimum flocculation. Farrow and Swift (1996) demonstrated that the jar test has several problems. It is important to realize that adsorption and flocculation are not separate sequential processes, but occur simultaneously (Hogg, 1999). The commonly used improved experimental procedure includes addition of the flocculant to a vigorously agitated suspension which is immediately stopped after addition of the reagent (Keys and Hogg, 1979). Different mixing/polymer addition conditions may result in very different floc sizes and settling rates. Owen et al. (2009) showed that mixing of the slurry with a dilute flocculant solution within the feedwell determines the performance of commercial thickeners. It was also shown that under certain conditions intense agitation for short times may even change the nature of flocculation, from total flocculation to a selective flocculation of only some mineral constituents (Ding and Laskowski 2007).

The vast majority of commercial flocculants are based on partially hydrolyzed polyacrylamide. As a result of hydrolysis even "nonionic" polyacrylamides contain some anionic groups. This is expressed as "degree of anionicity" (the degree of anionicity of completely hydrolyzed polyacrylamide is 100%, so it is a polyacrylic acid).

The effectiveness of polymers as flocculants depends on their molecular weight, the sign of their charge (e.g. anionic or cationic) and the relative charge density (for polyacrylamides this is expressed by degree of anionicity). Recent data (Xu and Cymerman 1999) indicate that the best flocculants for the Syncrude tailings (mostly clays) were moderately anionic high molecular weight polyacrylamides (optimum around 20-30% anionicity). This agrees very well with Ferrera et al.´s (2008) results. Henderson and Wheatley (1987) demonstrated a very strong effect of intrinsic viscosity (that is indirectly molecular weight) on sedimentation rate of flocculated tailings for polyarylamides with varying anionicities.

Another important group of flocculants is polyethylene oxide, $(-CH_2CH_2O-)_n$. Scheiner et al. (1985) showed that PEO can be successfully applied in dewatering coal-clay waste from coal preparation plants. The process requires the use of calcium (lime) or magnesium salts, and PEO. Their results strongly indicate the need for prior coagulation before efficient bridging by flocculant can occur. In this process lime is added up to pH 9 or higher and the PEO dosage required to get optimum results varied from 50 to150 g/Mg. Our results confirmed that different flocculants require different hydrodynamic conditions for best flocculation (Sworska et al., 2000).

In many countries water has become a scare commodity. The lack of fresh water in the area of Atacama Desert (Northern Chile) is forcing the copper industry to utilize seawater. Salinity of seawater is approximately 3.5%, and NaCl concentration is around 0.5 M, with important secondary ions such as: sulfate ions (2.7 g/kg); magnesium ions (1.29 g/kg); calcium ions (0.41 g/kg); bicarbonate ions (0.145 g/kg); etc. Traditionally seawater has been considered of low metallurgical quality for the flotation of Cu-Mo sulfide ores, and a desalination stage was believed to be necessary. This is true when the same flotation technology which is used with fresh water is applied with seawater. Consequently, the main challenge in the flotation of Cu-Mo-Au ores is the successful use of seawater without desalination in copper mineral processing mills. This will also require better understanding the effect of electrolytes on flocculation.

It can be expected that increased concentration of electrolyte may affect many flocculation sub-processes:

- it destabilizes suspension by coagulation improving the overall effect of the flocculant;
- it affects the conformation of the flocculant macromolecules in the solution;
- it affects adsorption of polymer macromolecules onto solid particles, and it affects flocculant overall ability to flocculate that is to bridge suspended particles;
- because of the presence of Ca^{2+} and Mg^{2+} ions in sea water other flocculants than PAM may be better in this environment (for instance PEO).

Some of such effects have been studied, mostly for the systems encountered in potash ores flotation, the process in which sylvite (KCl) is separated from halite (NaCl) by flotation in KCl-NaCl saturated brine (6-7 mole/dm^3 solution). The effect of carboxymethyl cellulose ($M = 2.5 \cdot 10^5$ Da) on stability of mineral suspensions under such conditions was studied by Pawlik et al. (2003), and the effect of guar gum ($M = 1.39 \cdot 10^6$ Da) by Pawlik and Laskowski (2006) which was followed by Ma and Pawlik (2007). Preliminary results for polyacrylamide flocculants were reported by Ferrera et al. (2009).

In order to study such effects on flocculation we found it necessary to first optimize experimental procedures utilized in studying efficiency of flocculation. The use of a shear vessel (similar to rotational Couette viscometers) in assessing flocculation efficiency has the advantage of quantifying the mixing intensity through the shear rate. The shear vessel in the past was used to study coagulation and was also used in the flocculation studies (Farrow and Swift 1996). Rulyov (1999, 2004) and Rulyov et al. (2005a, 2005b, 2009) has shown that the contacting diluted flocculant solution with the suspension in the shear vessel can: (1) vastly improve flocculant efficiency, and (2) allow studying the effect of hydrodynamic conditions on flocculation.

Farrow and Swift (1996) constructed their shear vessel with concentric cylinders of 200 and 210 mm in diameter and 120 mm in length. At the bottom of the vessel a glass tube 14 mm in diameter and 220 mm in length is used to measure the settling velocity. The experiments were made at a constant rotational velocity of 200 rpm. The outflow of the shear vessel was introduced immediately in the settling column. The authors concluded that the combination of shear vessel and settling column overcame most of the problems associate with jar test, in particular the strong dependence of batch settling test on mixing rate and cylinder diameter.

Using shear vessel Rulyov (1999) and Rulyov et al. (2000) have shown that the mixing time in flocculation can be reduced down from minutes to 5-6 seconds by the appropriate hydrodynamic treatment of the suspension at a given shear rate. This treatment, termed “ultra-flocculation” (Rulyov 2004; Rulyov et al 2005), ensures that not only flocculant molecules distribute fast and evenly within the suspension and adsorb on the surface of the particles, but also provides the formation of large and dense flocs. Depending on the size, size distribution and density of the particles in the dispersion, as well as on their volume concentration, the optimum values of the mean shear rate γ may vary in a wide range $300< \dot{\gamma} <5000$ s^{-1}. The significant advantage of ultra-flocculation is that it ensures a good mix of small and large particles in flocs before they get into the settling tube, thus providing for fast sedimentation and high degree supernatant clarification (Rulyov et al. 2009).

2. Experimental

In this work an instrument known as *UltraflocTester*, that combines a shear vessel with variable shear rate and an optoelectronic device (similar to the one developed by Gregory and Nelson (1984)) that measures the mean-root-square fluctuation of intensity of light beam passing normally through transparent tube while the formed flocs pass through tube are used to analyze the relationship of flocculation efficiency (or mean flocs size) with solid concentration, flocculant dosage and shear rate.

2.1. Material, experimental set-up and method

Flotation tailings from one of the major copper flotation plants in Chile, were used in all experiments. Solid volume fraction varied over the range from 1.8 to 15 %; material density was 2700 kg/m^3. An average particle size x_{50}=20 μm with size distribution characterized by x_{80}=40 μm and x_{20}=20 μm was determined using a

Sympatec Helos-Rhodos laser dispersion instrument. Orifloc-2020 polyacrylamide was applied as a flocculant. The set-up used to perform ultra-flocculation tests is shown in Figs. 1 and 2.

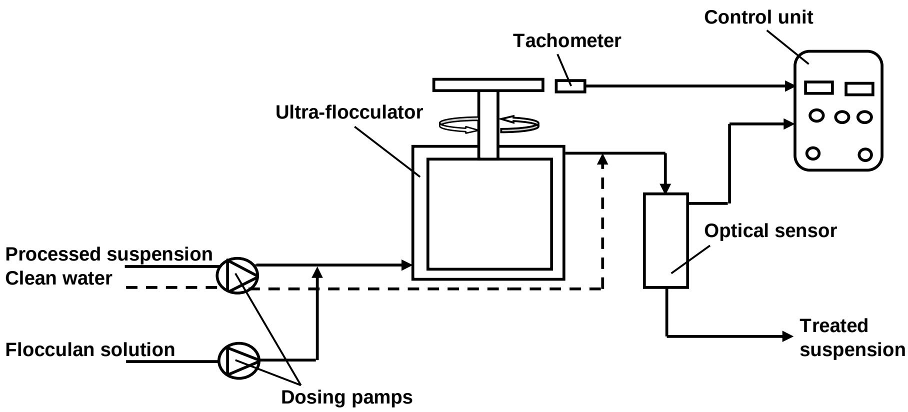

Fig. 1. Schematic illustration of the UltraflocTester, UFT-TFS-029

Fig. 2. Photograph of the UltraflocTester: UFT-TFS-029, Turboflotservice Company

It consists of a small shear vessel, referred to as ultra-flocculator in Fig.1. This Couette reactor, with a rotating cylinder of 28 mm and a gape of 1.5 mm was fed continuously with the suspension of tailings by a positive displacement pump. Before entering the Couette reactor the pulp receives continuously a dilute flocculant solution, at a flow-rate to give a pre-determined dosage. After 6 seconds conditioning at a pre-determined shear rate, the flocculated suspension is discharged from the instrument through a 3 mm inner diameter transparent tube equipped with an opto-electronic sensor which registers the fluctuation of intensity of light beam passing normally through mentioned transparent tube (in accordance with techniques proposed by Gregory and Nelson 1984). The electronic signal is processed and displayed in a three digital format thus showing in relative units the values of flocculation efficiency (or mean flocs size) and the mean shear rate $\dot{\gamma}$.

The different operational conditions were obtained by changing the flocculant feed rate and the shear rate while maintaining a constant feed rate of suspension to the instrument. When the feed suspension concentration exceeded the threshold for its optical analysis capacity, (φ_0=6%), it was diluted by introducing clean water between the shear reactor and the optoelectronic sensor (shown by a dash line in Fig. 1). In the tests designed to measure settling rate of the treated suspension, dilution was not used. In this case the suspension from the outlet of the tester was continuously fed to a small settling cylinder 14 cm^3 in volume and, as soon as the suspension filled the cylinder, it was allowed to settle and the initial settling velocity was recorded.

3. Results and discussion

The operational conditions of the experiments and the output of the instrument are given in Table 1.

Table 1. General data

Solid concentration [g/dm^3]	Solid concentration % by volume φ_0	Settling Velocity V_{opt}/V_{100} [mm/s]	Shear rate $\dot{\gamma}$ [s^{-1}]	Flocculant dosage [g/Mg]	$C_s \cdot V_{opt}$ $10^{-4} \cdot$[$g/cm^2 \cdot s$]	F_{opt}/F_{100} $10^{-4} \cdot$[m/s]
50	1.8	20/14	600	10	1000	3.72/2.60
100	3.7	13.6/9.0	500	8	1360	5.03/3.51
200	7.4	2.26/1.50	350	16	452	1.67/1.11
300	11.1	0.50/0.24	300	10	150	0.51/0.27
405	15.0	0.15/0.07	600	20	60	0.22/0.10

In Table 1 V_{opt} and V_{100} stand for the initial settling velocity after treatment at optimal shear rate $\dot{\gamma}_{opt}$ and at shear rate equal $\dot{\gamma}$ =100 s^{-1}, F_{OPT} and F_{100} are the corresponding solid-flux densities.

3.1. Effect of flocculant dosage on the efficiency of flocculation

The flocculation was carried out over 6 seconds at optimal values of the mean shear rate $\dot{\gamma}$, for the respective suspension concentrations (see Table 1).

Figure 3 demonstrates that the flocculation efficiency (relative floc size) increases monotonically with flocculant dosage, reaching 90 relative units with a dosage of 10 g/Mg for the low range of particle concentration and 20 g/Mg for the higher range. The observed increase in the flocculant dosage with the increase of the suspension concentration can most likely be attributed to the slowdown of the process of the flocculant macromolecules distribution within the volume of the suspension with increased solid concentration.

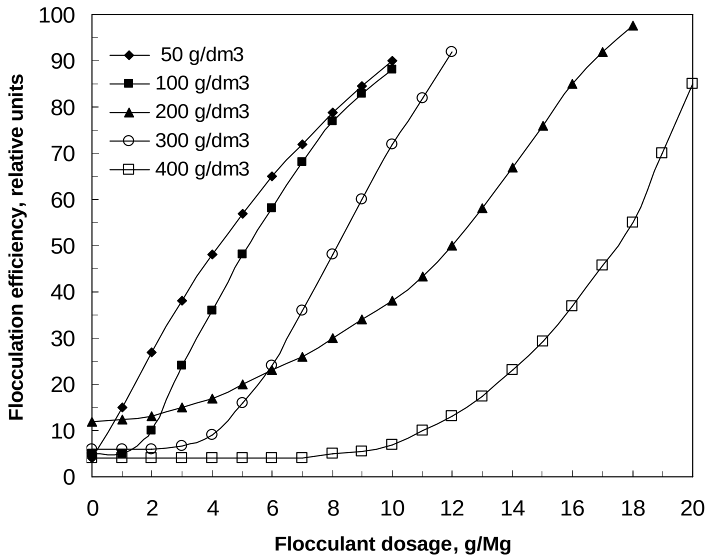

Fig. 3. Flocculation efficiency (relative mean floc size) versus flocculant dosage with the solid volume concentration as parameter

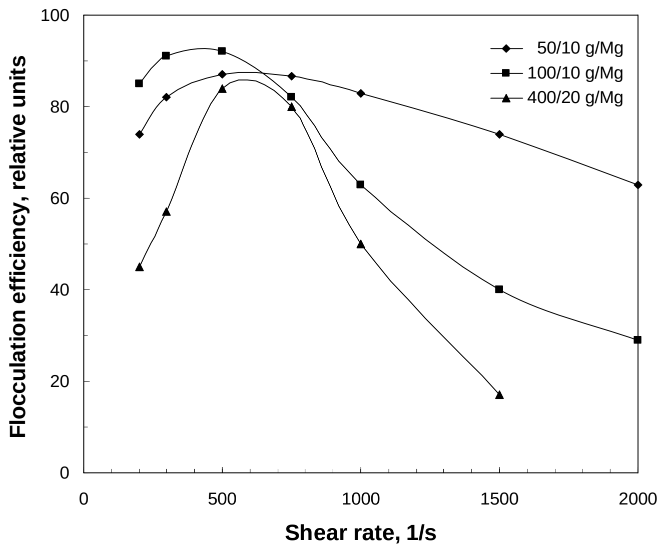

Fig. 4. Effect of average shear rate on flocculation efficiency (mean flocs size) for a different solids volume concentration (%) / flocculant dosage (g/Mg)

Figure 4 shows the effect of shear rate, $\dot{\gamma}$, on the flocculation efficiency, These results clearly demonstrate that maximum exists between 400 to 600 s^{-1}, depending on the solid concentration, with increasing values for higher concentrations.

The shift of the maximum of flocculation efficiency to higher shear values for higher flocculant dosages may be due to increased strength of the bridges bonding particles within flocs. As it was shown by Rulyov et al (2005), it allows for the formation of larger and stronger flocs.

3.2. Effect of the shear rate on the settling velocity

Since the shear rate influences the flocculation efficiency in the way expressed in the previous section, one would expect similar influence on the settling velocity. This was confirmed as shown in Figures 5.

The results given in Figure 5 indicate that the optimum shear rate corresponding to the maximum flocculation efficiency also corresponds to the maximum initial settling rate of the flocculated suspension. This confirms that the ultra-flocculation test is an effective method for identification of the optimal flocculation conditions.

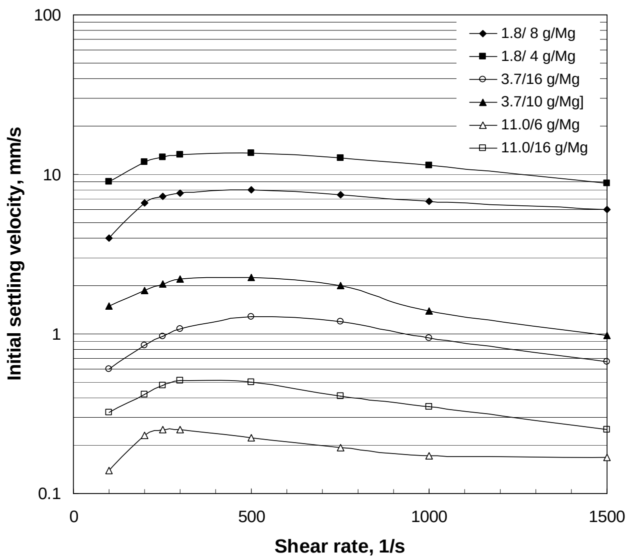

Fig. 5. Initial settling velocity versus average shear rate for a different solids volume concentration (%)/flocculant dosage (g/Mg)

3.3. Effect of the solid volume concentration on the optimal shear rate

It is important to establish the optimum solid concentration for flocculation in a commercial thickener. In the majority of industrial thickeners flocculation takes place in the feedwell where the feed is diluted with circulating water. Knowing the solid concentration that gives the best flocculation should permit calculation of the water dilution flow rate.

Figure 6 shows the effect of suspension volume concentration on the optimum shear rate for a given flocculation. Since the shear rate required for a good flocculation initially decreases with solid content, but increases again if the solid volume content is further increased, the minimum appears on the relationship between shear rate and solids content. Therefore, for the most efficient flocculation each solid concentration in the pulp requires selection of the optimum shear rate.

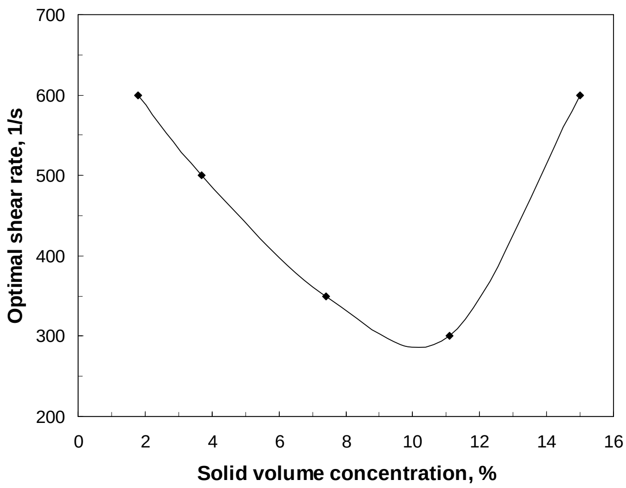

Fig. 6. Optimal average shear rate versus suspension solid volume concentration.

This relationship between shear rate and solids concentration can be explained using Smoluchowski theory, because at a given suspension concentration the floc size increases to maximum within a short time interval. On the other hand, with the increase in suspension concentration the distribution of flocculant macromolecules within the volume of suspension slows down. In particular, this is confirmed by increased consumption of the flocculant with the increased suspension concentration at a constant time interval. However, due to convective diffusion, with increasing shear rate the rate of flocculant molecules dissemination in the suspension significantly increases, leading to the growth of the dependence of the optimum shear rate on concentration in the region of large concentration values. This may also lead to some decrease in the required flocculant dosage as shown by Rulyov et al (2005).

4. Summary

In this project the results were obtained in the tests carried out with the flotation tailings from one of major Chilean copper flotation plants using a commercial polyacrylamide flocculant utilized by this industry. The results indicate that with the use of ultraflocculation the efficiency of the radial thickener can be increased by more than 1.5 times.

The results reported in this paper are part of the larger project aimed at utilization of sea water in flotation of Cu-Mo sulfide ores and must also answer the question on the effect of sea water on solid/liquid separation. Since polymer adsorption and flocculation are not separate sequential processes but occur simultaneously the performance of the flocculant very strongly depends on physical variables (agitation intensity, rate of flocculant addition, solids content, concentration of polymer stock solution, etc.). It is therefore of primary importance to use the proper experimental procedure in the studies on the effect of "goodness of solvent" on flocculation. The tests confirmed that the ultra-flocculation procedure, and UltraflocTester UFT-TFS-029, can conveniently be utilized to find optimum hydrodynamic conditions under which the effect of the goodness of solvent on the flocculation in processing flotation tailings from Chilean copper industry in sea water can be studied.

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