Flocculation of Fine Particles in Ceramic Wastewater by Using Polymers

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Summary

The clarification of industrial wastewaters by solid–liquid separation techniques and the removal of suspended particles are the problems of growing environmental consciousness. However, there appears to be very limited number of studies reported in the literature to investigate the flocculation and settling properties of ceramic wastewaters.
The efficiency of solid/liquid separation may be greatly improved by the application of synthetic polymeric flocculants, particularly in mineral processing plant where sedimentation, filtration and centrifugation processes are extensively used. In ceramic plants, the water used in ceramic processing is contaminated with suspended quartz, feldspar and associated clay particles, which results in a so-called wastewater problem which have to be dealt with from an environmental point of view.
In this study, sedimentation of ultrafine particles from ECE Ceramic Co. (Çorum/Turkey) ceramic wastewater sample was investigated using three anionic polymeric flocculants (Superfloc A-130, Superfloc A-100 and Enfloc 330A). The performances of the flocculant in the experimental studies were assessed with the change in the interfaces height during sedimentation resultant. The best performance was obtained Superfloc A-130. At the dose of 60 g/t for A-130, the settling rate was shorter than 60 seconds.

Keywords: ceramic wastewater, sedimentation, flocculation, settling rate, polymer

Introduction

Solid–liquid separation or dewatering processes generally involve unique set of challenges because of the presence of colloidal particles of varying sizes, shapes, and specific gravities as well as solution chemistry of their environments. Currently the most common method for solid-liquid separation is the use of thickeners in which the solids settles out to form a bed, leaving a clear supernatant which can be recycled back to the plant. The settling rate during solid-liquid separation within a thickener is important as this influences the size of the thickener required and the rate at which water can be recycled back to the plant (Kominek and Lash, 1979; Deniz, 2013).

Flocculation of fine particle suspensions depends on a number of factors, which include type, molecular weight and charge density (ionization degree) of the flocculant, mineralogical composition and particle size of solid particles, pH and chemical composition of solutions. Flocculation of fine particles may occur by polymer bridging, charge neutralization, polymer–particle surface complex formation and depletion flocculation, or by a combination of these mechanisms (Gregory, 1985). The bridging mechanism requires that the polymer chains be adsorbed on the particle surfaces, with only a few points of attachment, with the bulk of the chains projecting into the surrounding solution for contact and adherence to other particles (Pearse and Barnett, 1980).

Nowadays, flocculants used for flocculation are non-ionic, anionic and cationic polymers. Non-ionic and anionic polymers cause to form big, fast sedimentation and fairly compact flocks. However, it is preferable to use higher molecular weight anionic or non-ionic polymers over cationic flocculants for sedimentation process. It is known through the literature that non-ionic polymers are usually used in acidic slurries and high molecular weight anionic polymers are used in alkali slurries (Sabah and Yeşilkaya, 2000; Deniz, 2015).

A major advancement was seen in the 1950s when polyacrylamide flocculants were introduced. Early reference is made to application in water treatment in 1958 and they were certainly being used in the mineral processing industry in the early 1960s. The polyacrylamide molecule could be tailored to virtually every mineral processing situation and the next four decades saw massive expansion in its use. By substitution to the polyacrylamide chain, the addition of cationic and anionic functional groups gave polyelectrolytes which covered all slurry environments from mono-mineralic to multi-mineralic, low to high suspended solids, low to high dissolved solids and low to high pH. Manipulation of molecular mass from 5 to 25 million Da allowed successful application to be made on all types of solid–liquid separation equipment (Pearse, 2003).

Several studies have shown that high molecular weight anionic polymers (e.g. polyacrylamide) are commonly used in the settling of negatively charged clay (Scheiner and Wilemon, 1987; Hogg, 2000; Patience et al., 2003). In this case, the polymer bridging mechanism is of primary importance, whereas charge neutralization will be of secondary or little importance (Patience et al., 2003). The use of high molecular weight anionic polyacrylamide in flocculating negatively charged particles has the advantage of being more effective than cationic polymers by increasing settling rate and producing a distinct sediment structure, and in addition the re-stabilisation of clay particles by excessive polymer adsorption driven by strong electrostatic attraction may be avoided. The electrostatic repulsion between clay particles and the anionic polyacrylamide allows only limited polymer adsorption. On the other hand, the polymer molecule expansion arising from charge repulsion produces loops and tails, which lead to the formation of large open structure flocs. This effect has been seen to be effective in flocculating negatively charged clay dispersions (Somasundaran and Moudgil, 1988).

In this study, the dewatering of ceramic plant tailings belongs to ECE Ceramic Co. from Çorum, Turkey was investigated using a sedimentation technique.

Material and Methods

Material

The ceramic wastewater sample was collected as dilute (8.5% solids by weight) from the discharge of fine tailing in the ECE Ceramic Plant (Çorum/Turkey) and used for laboratory scale tests. Total amount of samples used in the laboratory tests were about 150 litres. The solids of the fines fraction (-106 μm) are a mixture of clay minerals, quartz, albite and kaolinite, and other finely divided minerals (as calcite).

Methods

The chemical composition of tailings solid was analyzed by X-ray fluorescence, and the particle size distribution was determined using Malvern Mastersizer Particle Size Analyzer. The mineral composition was determined by X-ray diffraction (XRD). The pH was measured with a lab pH Meter.

The flocculation experiments were carried out using a mechanical mixer with a speed control.

For each test, 500 mL of original slime wastewater containing 8.5% w/w solids was placed in a 600 cm^3 glass measuring cylinder and stirred for 2 minute at a rotational speed of 500 rpm to ensure homogeneous dispersion. The required amount of polymer solution was added continuously into the suspension during the stirring, which was stopped after optimum mixing time.

Experimental

A base case natural settling test on the samples was performed in order to highlight the problem areas of material type and depths. The anionic polyacrylamide flocculant, Superfloc A-100 and A-130, an acrylamide– acrylic acid copolymer was obtained courtesy of Cytec, USA. Addition, Enfloc 330A, a synthetic flocculants of high molecular weight based on polyacrylamide, was obtained Sebit Chem Co., Korea. A 0.5% by weight polymer solution was made up by adding dry polymer powder to the vortex of a stirred solution followed by high speed mixing for 1 h. The solution was then mixed on an end over end mixer for 12 h. The solution was then rested for a further 12 h prior to use. All polymers solutions were used 24–48 h after make up. Suspensions were diluted in tap water.

Polyacrylamide addition, the suspension was mixed for 20 sec, and thereafter the prepared ceramic tailing suspensions were transferred to 600 ml measuring cylinders (60 mm in diameter). The height of the slurry and water interface was recorded as a function of time and used to calculate the settling rates of the flocculated suspension.

Results and Discussion

Mineralogical Analysis

XRD analysis of the ceramic tailings was indicated that

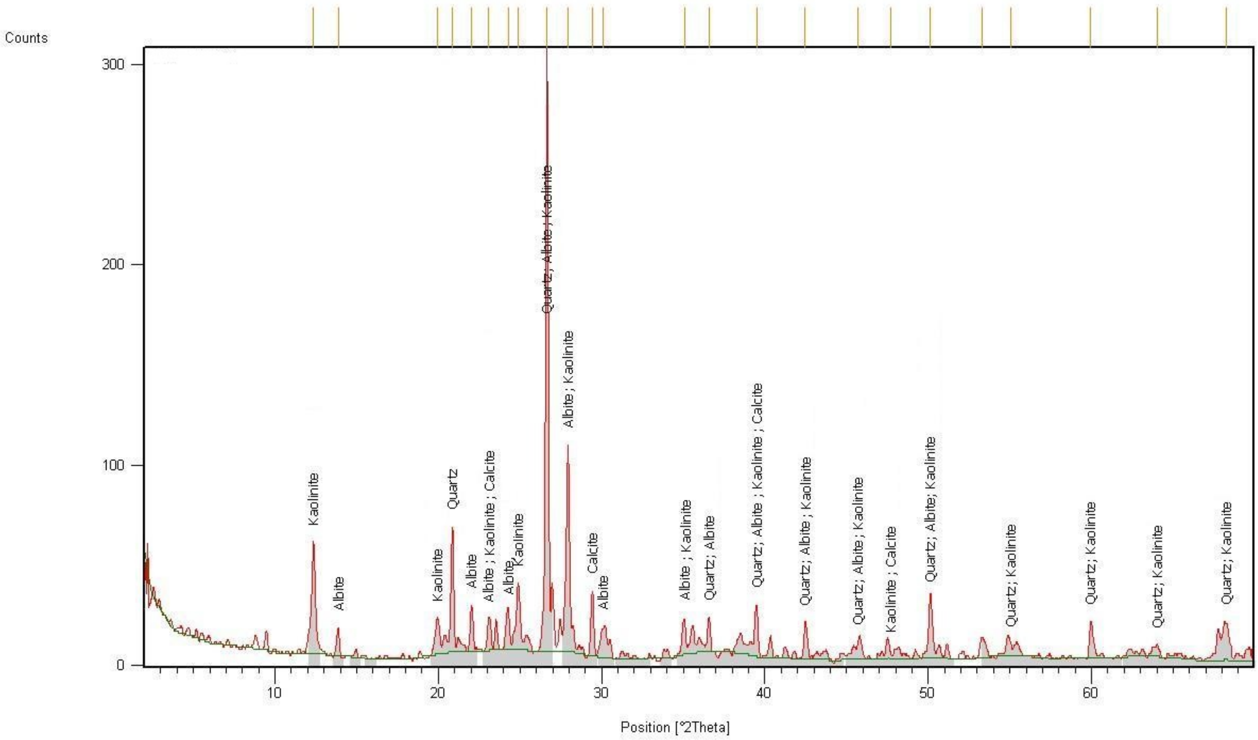

Fig. 1 XRD peaks of particles from ceramic wastewater

Rys. 1 Wartości maksymalne XRD dla ścieków z przemysłu ceramicznego

Tab. 1 Chemical compositions of ceramic tailing

Tab. 1 Skład chemiczny odpadów ceramicznych

Components	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LOI
%	60.12	25.33	1.27	0.12	0.85	3.09	0.98	8.04

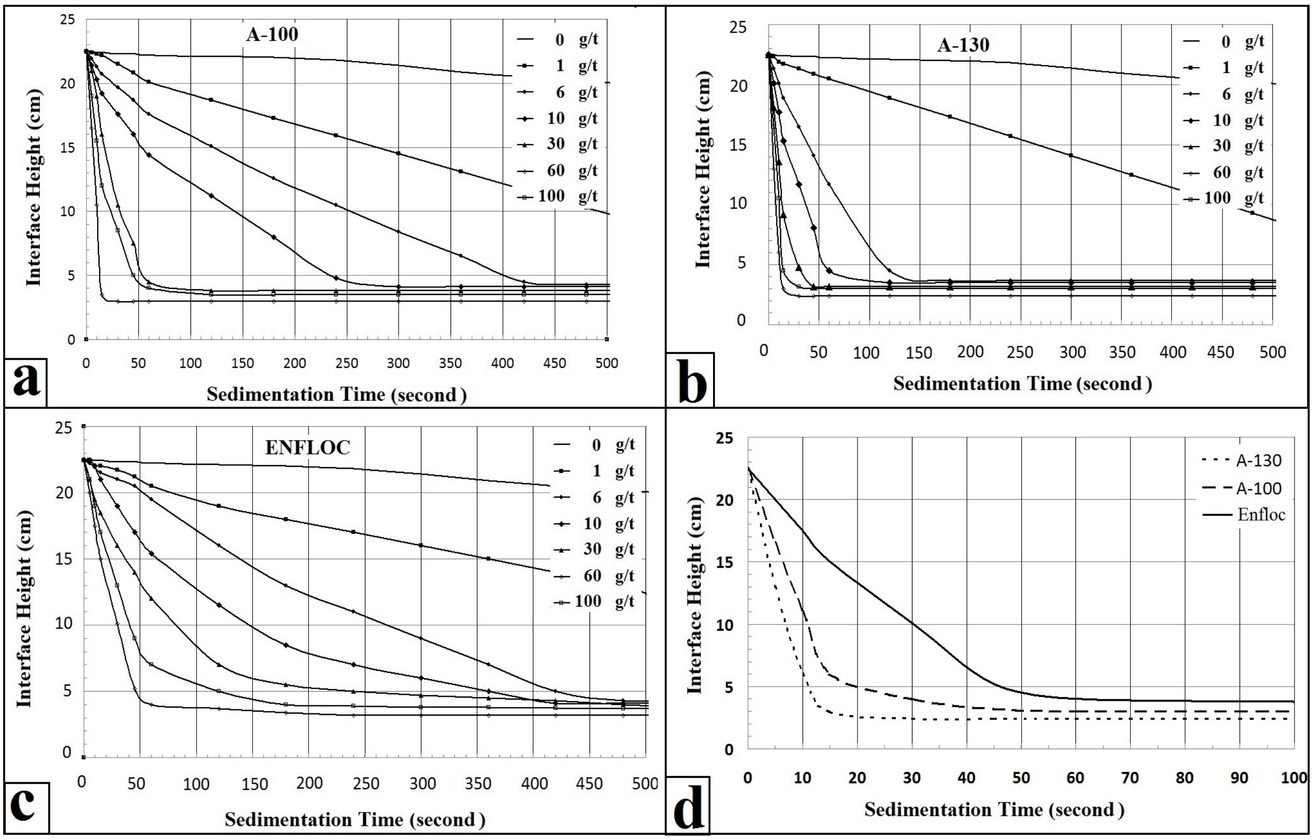

Fig. 2 Sedimentation curves with different polymer dosage in using [a] Superfloc A-100 [b] Superfloc A-130 [c] Enfloc 330A and [d] comparision of sedimentation curves as different flocculant types

Rys. 2 Krzywe sedymentacji dla różnych dawek polimerów: [a] Superfloc A-100 [b] Superfloc A-130 [c] Enfloc 330A oraz [d] porównanie krzywych sedymentacji dla różnych typów flokulacji

the main minerals are quartz, albite and kaolinite (Figure 1).

Chemical analysis

The chemical compositions of the associated minerals in ceramic wastewater were determined by XRF method as shown in Table 1. As expected, the tailings are mainly composed of SiO_2 and Al_2O_3.

Particle size distribution

The average particle size determined from the Gaudin-Schuhman type of plot was 13.74 µm, and the percentage of slime size (<20 µm) was constituted 63.62% of the overall material. Based on the Wentworth classification (Wentworth, 1922), although the percent of particles in clay size accounts for 18.65% (<4 µm), the percentage of particles in silt size is 78.17% (4–95 µm). Those particles in sand size were 3.18% (>95 µm). If dosage is increased, it is observed that flocks are disintegrated.

Zeta potential tests

Because of the high ionic strength (or high conductivity) of ceramic tailing, zeta potential of particles from the wastewater was not measured directly. Instead, original tailing was dried at first, and then test solution was prepared with distilled water. The zeta potential measurements for the fine particles were made by a Malvern zetameter device using laser Doppler velocimeter principle. The using double distilled water was used for preparation of solid suspension in 0.1% solid. As apparent, there is no zero zeta potential value (zpc) indicating the iso-electric point (iep) at different pH values adjusted. The highest zeta potential (35.2 mV) was measured in the neutral pH (8.54) indicates that the suspension is quite stable. pH of the solution was adjusted by adding HCl and NaOH inside test solution.

Sedimentation tests

The flocculation tests were performed in the presence of three type polymers (Figure 2 [a,b and c]) at different dosages. Figure 2d had shown behaviour at optimum polymer dosages for ceramic tailings. Addition, the tests performed with three flocculants showed relationships between settling rate and flocculant dosage (see Figure 3).

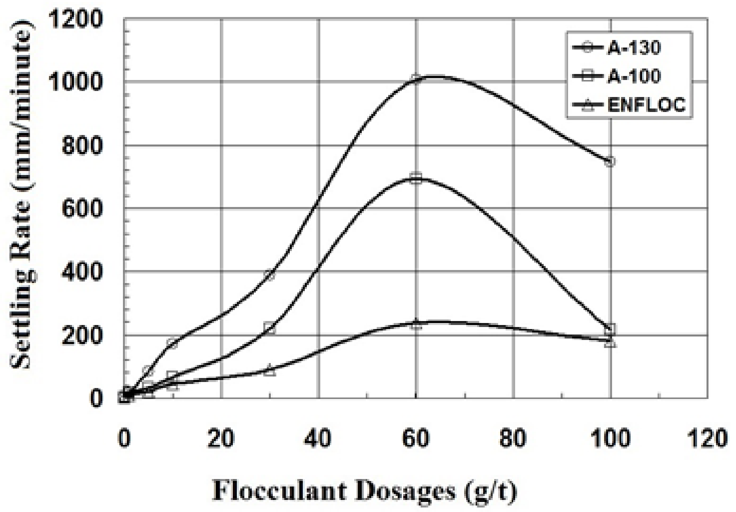

Fig. 3 Effect of flocculant dosages on settling rate for different flocculant type

Rys. 3 Wpływ dawek flokulantów na sedymentację dla różnych flokulantów

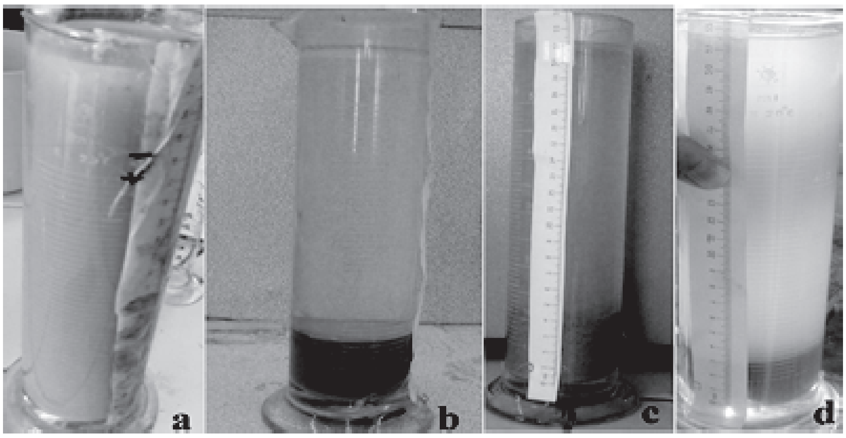

Fig. 4 Results for settling tests after 30 minute for various test samples a) natural settling, b) A-100 c) A-130 and d) Enfloc 330A]

Rys. 4 Wyniki testów sedymentacji po 30 minutach dla różnych próbek a) sedymentacja naturalna, b) A-100 c) A-130 oraz d) Enfloc 330A

As it can be seen Figure 3, the settling rate increased with increasing polymer dosages for three polymer types. For each three flocculants, settling rate reached a maximum at around 60 g/t polymer dosage, and then began to decrease with increasing polymer dosage. At low dosages, the floc size is expected to be very small because of insufficient amount of polymer adsorption on particles. The increase in the amount of adsorbed polymer results in the incorporation of more suspended particles in the floc and in turn enlargement of the floc size, leading to the enhanced settling rate. Figure 3 clearly shows that in most polymer dosages, settling rates of Superfloc flocculants are higher than Enfloc 330A flocculant. Addition, Superfloc A-130 shows very much better performance than Superfloc A-100. In other words, at the approximately same polymer dosage (60 g/t), Superfloc 130 was produced larger flocs. As settling rate values, whereas highest settling rate of Superfloc A-130 has 1008.25 mm/min and A-100 has 692.47 mm/min, on the other hand, Enfloc 330A has 239.57 mm/min settling rates.

Figure 4 provided, the photographic description of settling behaviour of flocculant dosed in 600 ml measuring cylinder sets. The natural settling behaviour of ceramic wastewater is photographically and schematically illustrated in Figure 4(a). In this condition, there is no, clear distinct interface between the accumulated sediment bed and overlying water, thereby the volume fraction at the top of the accumulated sediment cannot be considered as gel point (see Figure 4a).

Seen from Figure 4b, Figure 4c and Figure 4d, at using flocculants (Superfloc A-130, A-100 and Enfloc 330A) there is very rapid settlement, leading to the formation of a coarsely structured matrix of deposited solids. The settlement properties of this solids column appear to be largely insensitive to dose. Through time this layer slowly reduces in height as water is gradually released due to compressive settlement of the solids matrix.

Conclusions

Present day developments for polyacrylamide-based flocculants and those of the future are likely to be based on the "molecular architecture" concept. This will enable flocculant technology to produce the performance required to meet the increasing and changing demands for solid–liquid separation in the ceramic processing industry (Deniz, 2015).

Characterization of ceramic tailings using a XRD technique reveals that the tailings are mineralogically composed of quartz, albite and kaolinite. The tailings exhibit negative charge at all pH values with no apparent zero point of charge. The highest zeta potential (-35.2 mV) was observed at neutral pH (8.54). The average particle size determined from the Gaudin-Schuhman type of plot was 13.74 μm, and the percentage of slime size (<20 μm) constitutes 63.62% of the overall material.

The flocculation tests were performed in the presence of different types of polymers at different polymer dosages. The settling rate increased with increasing polymer dosage and reached a maximum at highest polymer dosage for all polymer type, settling rate reached maximum at 60 g/ton-solids polymer dosage then began to decrease with increasing polymer dosage.

In most polymer dosages, Superfloc A-130 settling rates were higher than others. It is clear from the results that A-130 shows quite better performance than other flocculants. On the other hand, relatively small flocs and the lowest settling rate was obtained by the high anionic flocculant Enfloc 330A.

In conclusion, the clarification of ceramic wastewater by polyacrylamide flocculants was achieved within 0.5-1 minute as against the natural settling time of 1-2 h.

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Flokulacja drobnych cząstek w ściekach ceramicznych przy użyciu polimerów

Klarowanie ścieków przemysłowych technikami rozdzielania substancji stałych i ciekłych oraz usuwanie zawieszonych cząsteczek jest problemem rosnącej świadomości ekologicznej. Jednakże okazuje się, że istnieje bardzo ograniczona liczba przedstawionych w literaturze badań dotyczących flokulacji i właściwości osiadania ścieków ceramicznych.
Efektywność separacji ciało stałe/ciecz, może być znacznie poprawiona przez zastosowanie syntetycznych flokulantów polimerycznych, zwłaszcza w zakładach przetwórstwa minerałów, gdy szeroko stosowane są procesy sedymentacji, filtracji i wirowania. W zakładach ceramiki, woda stosowana w obróbce wyrobów ceramicznych zanieczyszczona jest przez zawieszony kwarc, skaleń i związane cząstki gliny, co prowadzi do tak zwanego problemu ścieków, które muszą być rozpatrywane z punktu widzenia ochrony środowiska.
W badaniu tym, sedymentacja cząstek ultradrobnych z próbki ścieków ceramicznych z ECE Ceramic Co (Çorum, Turcja) została zbadana z zastosowaniem trzech polimerowych flokulantów anionowych (Superfloc-130, Superfloc 100 i Enfloc 330A). Charakterystyka działania flokulantu w badaniach doświadczalnych była oceniana za pomocą zmiennej wysokości interfejsów podczas sedymentacji końcowych. Najlepsze wyniki uzyskano z użyciem Superfloc A-130. Dla dawki dawce 60 g A-130/t, szybkość osadzania była krótsza niż 60 sekund.

Słowa kluczowe: ścieki z przemysłu ceramicznego, sedymentacja, flokulacja, wskaźnik sedymentacji, polimer