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Effect of pH and polymer charge density on settling rate and turbidity of natural stone suspensions

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Abstract

In the present paper, the effects of suspension pH and charge density of anionic polyacrylamide (PAA) on flocculation behavior of two different natural stone suspensions (NSS) marble and travertine were investigated by settling rate and turbidity as indicators. The flocculation of NSS occurs even when the natural stone (NS) powders and the flocculants carry the same sign of the charge. The polymer bridging mechanism is responsible for flocculation of marble and travertine suspensions. The settling rate of NSS exhibits an optimal balance between the flocculating power of the polymer resulting from its expanded position in suspension due to its anionicity degree and the repulsive forces between the negatively charged NS powders and anionic flocculants. At high pH of 11, the settling rate of both natural stones increased significantly with each polymer except the 40% anionic polymer. In contrast, at low pH of 6, the supernatant turbidity of both suspensions was at the minimum level with no significant difference between them. However, when considering the settling rates, each polymer except the nonionic one showed different flocculation performances. The settling rate and turbidity results are analyzed in the light of zeta potential data to identify the mechanism of polymer uptake onto NSS.

Keywords: flocculation; natural stone suspension; polymer; polyacrylamide; marble; travertine; suspension pH; turbidity; settling rate; wastewater

1. Introduction

In natural stone (NS) factories, marble cutting and polishing requires a large amount of water which is reused in the factory upon decantation in wastewater ponds. Cutting of a marble block, for instance, produces approximately a part of 30–40% in weight of the block as fine powder (Önenç, 2001). Relatively large sized particles of the powder settle by gravitational forces through canals but finely sized (−0.1 mm) particles move with water. This suspension consisting of NS powders and water is treated by solid–liquid separation using flocculation and filtration and the water is recycled. The presence of suspended particles particularly larger than 50 μm in the recycled water may cause polishing problems during NS processing (Acar, 2001). In addition, the

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suspended particles may results in pipe clogging. Failure in selecting a suitable flocculant may result in decrease in polishing and cutting recovery due to the presence of free polymer molecules in recycled water.

Settling rate and turbidity are indirect but provide a simple way to measure the performance of a flocculation process, and are governed by the floc size distribution. The floc size distribution can generally be controlled by proper flocculant selection and appropriate use of flocculant addition and mixing conditions (Hogg, 2000). For a successful flocculation, suspension parameters such as pH, ionic strength, temperature, type of flocculants and its properties such as molecular weight, charge density, and molecular structure are important (Werneke, 1979; Atesok, 1988; Hogg, 2000; Yarar, 2001). Accordingly, an appropriate polymer formulation together with suspension conditions especially pH must be optimized.

Natural stones such as travertine and marble consists of over 90% calcite ($CaCO_3$), thus can be considered as a carbonate mineral. However, when their surface properties especially zeta potential (ZP) (Fig. 1), associated impurities (i.e., coloring metal oxides Fe_2O_3, TiO_2 or other metal oxides MgO, Al_2O_3), and geologic formation are considered, they may indicate some physical, chemical and mechanical differences with regard to the pure calcite mineral. Of course, there are some marginal differences between marble and travertine (Immib, 1997).

To the knowledge of author, there are only a few studies about the flocculation of NSS. Bayraktar et al. (1996) have worked on the flocculation of marble suspensions and determined that anionic polymer of

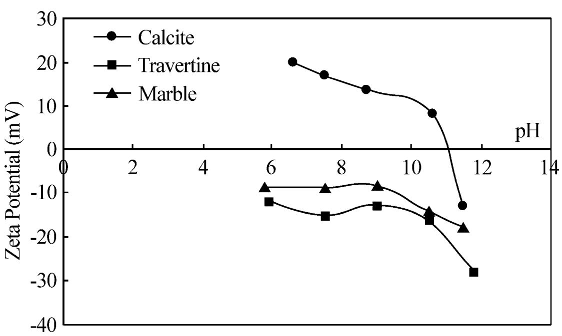


Fig. 1. Variation of zeta potential of natural stone powders and calcite mineral as a function of suspension pH in the constant ionic strength of 0.01 M NaCl.

high molecular weight (HMW) gave the best results for settling rate and water clarity. Seyrankaya et al. (2000) studied the effect of pH and polymer type on the flocculation conditions of marble and observed that there is no effect on its settling rate while the low charged anionic flocculant showed the best performance for both settling rate and water clarity. Nishkov and Marinov (2003) have shown that 31% anionic polymer gave the best settling rate on Bulgarian marble suspension. The influence of suspension pH and anionicity degree (or charge density) of polymer on floculation behavior of NSS was however not discussed in the above studies. In addition, no systematic study on the effect of charge density of polymer on flocculation of NSS appears in the literature. On the other hand, there are also a few studies on flocculation of calcite mineral. Yarar and Kitchener (1971) have studied on selective flocculation of minerals (quartz, calcite and galena) and found that agitation regime (stirring time and polymer addition method) have a significant effect on calcite flocculation. Likewise, a study by Friend and Kitchener (1973) on the selective flocculation of calcite from mineral mixtures (calcite–rutile, calcite–quartz) by anionic polymer in the presence of tripolyphosphate used as a dispersant for calcite reported that (i) HMW polymers have greater flocculating power, and (ii) flocculation can be prevented by providing a sufficiently strongly negative zeta potential on calcite surface. Nyström et al. (2003) examined the effect of cationic charge density and molecular weight of cationic starch of calcite dispersion and showed that the HMW starch with 20% cationic charge induced the strongest flocculation. In addition, particle size and surface area of particles and slurry flow rate on calcite slurry in a continuous system (linear pipe) had a marked effect on the flocculation.

In this study, the influence of suspension pH and the anionicity degree of flocculant on flocculation of NSS is extensively discussed in terms of settling rate and turbidity. Furthermore, the influence of the type of NSS on their settling rate and turbidity are evaluated.

2. Experimental

In the experiments two different NSS, marble and travertine suspensions, were used. The commodity

Table 1
Chemical composition of marble and travertine powders

Sample	Contents (%)							
	CaO	MgO	Fe_2O_3	SiO_2	Al_2O_3	Na_2O	K_2O	LOI
Travertine	54.35	0.42	0.20	0.17	0.85	0.03	0.20	43.75
Marble	54.25	0.22	0.20	0.70	1.15	0.03	0.20	43.20

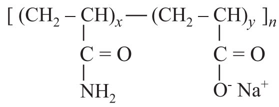
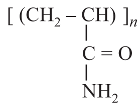
name of the natural stones are Denizli Travertine and Akşehir Black Marble (hereafter, they will be called as travertine and marble or natural stone), which were processed in marble factories in Afyon (Turkey) which is called the Marble City of Turkey. The marble slurry has been supplied from Gürel Marble and the travertine slurry supplied from Tureks. The two samples were taken in their original slurry state from the wastewater collector pool present previous to sedimentation tank and brought to our laboratory. The pH and solid ratio of the original travertine and marble slurry were 8.4 and 9.8, and 2.2% and 8.6% (w/w), respectively. They were passed through a 0.1-mm of sieve and dried at room temperature. The mineralogical analyses of these powder natural stone samples were characterized by XRD (Shimadzu-6000) using Cu Kα and almost all peaks represented a typical calcite ($CaCO_3$) mineral. The chemical analysis given in Table 1 was obtained by XRF method (Spectro X-Lab 2000). The particle size analysis determined by Fritsch Particle Sizer Analysette 22 and other physical properties of the samples are given in Table 2 (from Immib, 1997). Anionic flocculants in powder form used in this study have been supplied from Superkim Chemical of Turkey and manufactured by Ciba Specialty Chemicals (UK). The anionic flocculants Na-Polyacrylate (Na-PA) is made up of sodium acrylate–acrylamide copolymer and nonionic flocculant is made up of polyacrylamide (PAA) and their properties are given in Table 3.

Flocculation tests of marble and travertine powders were carried out in a 500-mL of graduated mixing cylinder using tap water. Prior to the flocculation tests 0.1% (weight/volume, w/v) stock solution of the flocculant was prepared with distilled water and diluted to 0.01% (w/v) before use. The NS suspension was prepared by addition and dispersion of 21 g of powder sample in 500 mL of tap water in mixing cylinder. Solid ratio of the suspension was selected as 4% (w/w), which is a medium value for the original NS slurries. Then, pH adjustment (only for pH 6 and pH 11) was made using 1 M NaOH and HCl solution. The pH measurements were made by Inco-lab pH-Meter. Afterwards, the desired amount of flocculant solution was taken and added to the suspension by an adjustable automatic pipette. The cylinder was sealed and inverted four times to obtain a good mixing, and put on a smooth ground to track the flocculated NSS. The settling rate of the flocculated suspension was determined by recording the height of the suspension/water interface as a function of time. As recommended by the flocculant manufacturer (Ciba) in the calculation of settling rate, a depth of 3 and 8 cm from the suspension surface was used. At the end of the 15 min settling period, a sample of 12 mL from the supernatant liquid was siphoned out from a depth of 12 cm and its turbidity was measured by Velp-115 turbidimeter which gives the turbidity result as Nepheleometric turbidity unit (NTU). The tap water used in the flocculation tests had the following properties: pH 7.3–7.5, turbidity 0.3 NTU, specific conductivity 1380–1450 μmhos/cm, including anions and cations as mg/L Cl^-114, F^-0.4, NO_2^-< 0.1, PO_4^{3-}< 0.1, SO_4^{2-}144, CO_3^{2-} <10, HCO_3^- 439, K^+ 9.6, Na^+ 93.6, NH_4^+ <0.1, Ca^{2+} 112, Mg^{2+} 33.5. From these, the ionic strength (I) of the NS suspension calculated as 0.02 mol ion/L by using the equation of "$I=1/2\Sigma C_i Z_i^2$" (Çelik and Ersoy, 2004). Where C_i is the concentration of an ion i in mol/L and Z_i is the valence number of i. The ions released from natural stone powders have been excluded in the calculation of ionic strength.

Table 2
Some properties of natural stone powders

Sample	Particle size (μm)			Porosity (%)	Bulk density (g/cm^3)	Mohs hardness
	90 wt.%	50 wt.%	10 wt.%			
Marble	<30	<8	<1.4	0.4	2.71	4
Travertine	<38	<10	<1.5	2.3	2.50	4

Table 3
Properties of the polyacrylamide-based anionic (sodium polyacrylate, Na-PA) and nonionic (polyacrylamide, PAA) flocculants of high molecular weight

Commodity name	Mol weight (g/mol)[a]	Degree of anionicity[a] (%)	Chemical structure of Na-PA and PAA
SPK 502[b]	15 million	18	
SPK 508[b]	15 million	28	
SPK 1111[b]	15 million	34	
SPK 504[b]	15 million	40	Na-PA
Magnofloc 351[c]	15 million	0 (zero)	 PAA

[b]: Given by Superkim (Turkey). [a], [c]: Given by the manufacturer firm, Ciba (UK).

The zeta potential (ZP) measurements of marble and travertine powders, and pure calcite minerals were made in distilled water of a constant ionic strength (0.01 M NaCl) by Zeta-Meter 3.0. Prior to ZP measurements powder sample was dispersed at 0.1% (w/v) solid ratio in distilled water, pH and ionic strength was adjusted to desired value and was stirred on a magnetic stirrer for 5 min at room temperature. Required amount of suspension was transferred into the electrophoresis cell of the zeta meter. During the ZP measurement 10 particles were tracked and the average of their ZP values was taken. Consequently, the ZP changes of travertine and marble as a function of pH were determined. The working principle of the zeta meter 3.0 is based on the electrophoresis method (Çelik and Ersoy, 2004) and it computes automatically the ZP using Smoluchowski equation.

3. Results and discussions

3.1. Zeta potential measurements

The zeta potentials of marble, travertine and pure calcite mineral versus the suspension pH were determined in Fig. 1. Surprisingly, the zeta potential curves of NS powders are very different from calcite mineral; that is, the isoelectrical point for neither marble nor travertine was obtained while calcite exhibited an isoelectrical point at about pH 11 as expected (Yarar, 2001). Here it must be noted that the zeta potential measurements were repeated three times, but due to excessive dissolution of NS powders and calcite at pH values lower than 6, their zeta potentials could not be measured. In addition, relative differences between marble and the travertine powders are seen in Fig. 1. Although differences between NS powders and calcite and also between NS powders could not be explained exactly, it may be attributed to impurities and surface contaminations during the NS processing. Since, the surface heterogeneity of minerals and undetected impurities may affect the zeta potential of minerals (Kulkarni and Somasundaran, 1976; Ersoy and Çelik, 2002).

3.2. Settling rate

The settling rate curves for travertine (Fig. 2A) and marble (Fig. 2B) suspension as a function of polymer dosage were obtained for each polymer against degree of anionicity (0%, 18%, 28%, 34% and 40% anionicity). It is clear that flocculation performance (as settling rate) increases with increasing charge density to a certain anionicity degree, but further increase in charge density leads to a decrease again in the performance. The polymer with 28% anionicity showed the best performance for travertine suspension while the polymer with 34% anionicity yielded the best performance for marble suspension. In travertine suspension, in order to reach to a 1500 mm/min of settling rate the required polymer dosage are 85, 35.7, 60, and 120 g/ton for the polymers of 18%, 28%, 34% and 40% anionic, respectively. In addition, in the presence of nonionic polymer 1500 mm/min of

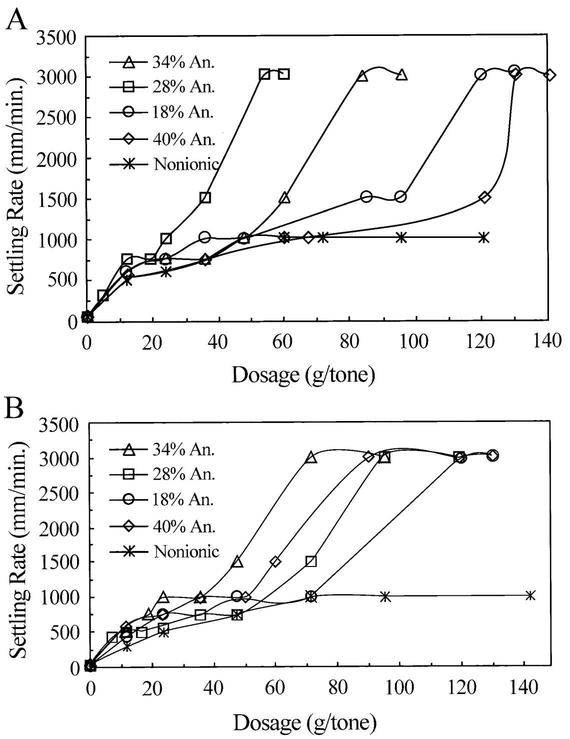


Fig. 2. Settling rate of flocculated travertine (A) and marble (B) suspension versus the flocculant's dosage which have different anionic charge at pH 7.5 (natural pH of the suspensions).

settling rate could not be reached. In marble suspension, 1500 mm/min of settling rate was reached at 88, 71, 47, and 60 g/ton of dosage for the polymers of 18%, 28%, 34% and 40% anionicity, respectively. Similarly, for nonionic polymer the settling rate of marble suspension could not reach this rate. Moreover, as seen in Fig. 2A and B, the settling rate of NSS increases with increasing polymer dosage, and at a certain dosage for each type of polymer, it reaches the maximum rate and remains constant at this rate.

On the other hand, Fig. 3A and B indicates the settling rates of travertine and marble suspensions, respectively, obtained at different suspension pH values of pH 7.5 (natural suspension pH), pH 6 and pH 11 for each type polymer at a constant polymer dosage of 35.7 g/ton. Except the 40% anionic polymer, the other polymers at high suspension pH (pH 11) enhanced the settling rate significantly for both NSS.

Looking at both Figs. 2A, B and 3A, B, it is possible to say that the polymer bridging mechanism operates on flocculation of NSS either travertine or marble suspension in the presence of HMW polyacrylamide-based anionic polymer. Since, the increase in the settling rate, i.e., the increase in floc size with increasing the degree of anionicity, results from the more expanded form of polymer chain, which enhances its flocculating power. Similarly, increasing suspension pH enhances the flocculating power of the polymers except 40% anionic polymer due to the same above reason. High pH can hydrolyze the nonionic amide groups (–$CONH_2$) of PAA or Na-PA and convert to carboxylate (–COO^-H^+) groups. Consequently, two adjacent negative groups repel each other leading to expanded chains. As well known from the literature the term of "expanded polymer chain" is the most important indicator of the presence of polymer bridging mechanism especially with HMW polymers (Friend and Kitchener, 1973; Werneke, 1979; Gregory, 1989; Yarar, 2001). The most important property of the polymer bridging mechanism is to produce large sized flocs and high settling rates (Hogg, 2000) because HMW polymers can adsorb on a

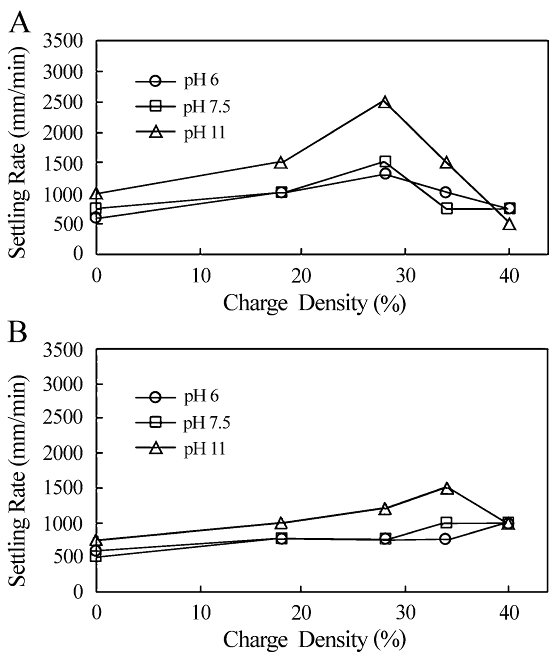


Fig. 3. The influence of suspension pH on the settling rate of the flocculated travertine (A) and marble (B) suspension at constant flocculant's dosage (35.7 g/ton).

number of particles at many points along the long polymer chain (Gregory, 1989).

However, an excess increase in the charge density causes long-range electrostatic repulsive forces between the polymer and negatively charged NS particles which adversely affect the flocculation power of the polymers. Hence, the settling rate of the NSS is reduced Similar trend has been obtained in the flocculation of coal tailings by PAA based anionic polymers (Werneke, 1979). In addition, the flocculation of marble suspension using PAA based anionic polymer of 31% anionicity has given the best settling rate (Nishkov and Marinov, 2003) in line with the results of this study. Unlike the present study, Seyrankaya et al. (2000) determined that the anionic polymer of the lowest anionicity (the degree of anionicity is not given) gives the best settling rate for marble (white marble) suspension.

Another important result inferred from Figs. 2A, B and 3A, B is that the flocculation of NSS by anionic polymers occurs even when the marble and the travertine particles, and the polymers carry the same sign of charge. Namely, the anionic polymers can adsorb (or attach) on these particles even when their net surface potential is negative. A similar case is also reported earlier on selective flocculation of synthetic calcite mineral by polyacrylic acid (Friend and Kitchener, 1973). This indicates that the sum of attractive forces between the negative NS particle and the anionic polymer outweighs the electrostatic or electrical double layer (EDL) repulsive forces. The possible attractive forces may be listed as follows: (i) local coulombic forces between the divalent metal cations (Ca^{2+}, Mg^{2+}) at the particle surface and the dissociated carboxyl (–COO^-) groups on the polymer chain. These cations can serve as an ion bridge between the polymer and the particle as well known from the kaolinite–polyacrylamid interaction (Stutzman and Siffert, 1977). (ii) Hydrophobic interactions between the nonpolar segments of polymer chain and the hydrophobic (nonwettable) areas on the particle surfaces. (iii) H-bonding between the amide (–NH_2) groups and the surface hydroxyl (i.e., –CaOH) groups. Indeed, H-bonding mostly are seen when nonionic polymers are used in flocculation systems but it is thought that this type bonding between NS particles and anionic polymer (Na-PA) of long polymer chain (mol weight of the polymers>10^6 g/mol) may occur due to the presence of surface hydroxyl groups on NS particles and presence of (–NH_2) groups on polymer chain (Pefferkorn, 1999; Werneke, 1979).

The main difference between the flocculation behavior of marble and travertine is that the former showed the best performance at 34% anionic polymer (Fig. 2B), whereas the latter showed at 28% anionic polymer (Fig. 2A). It is assumed that this can results from the differences in their zeta potentials. The zeta potential of travertine at pH 7.5 is about −15 millivolt (mV) while marble's zeta potential is about −9 mV (Fig. 1). Hence, further increase in polymer charge density especially after the 28% lead an increase in long-range EDL repulsive forces between the polymer and the travertine particles. This reduces polymer adsorption on travertine leading to weakness in polymer's flocculating power; this may in turn result in the breakage of large sized flocs during mixing. Consequently, the settling rate of flocculated travertine suspension decreases in the presence of 34% and 40% anionic polymer. But for marble suspension, these repulsive forces possibly become significant after 34% anionicity degree of polymer due to relatively low zeta potential of marble particles. Hogg (1999) also expresses that depending on the magnitudes of the charges (solid charge and polymer charge) the EDL repulsive forces between them may inhibit or even prevent polymer adsorption. The other important difference between the flocculation performance of NSS is that, e.g., to reach the settling rate of 1500 mm/min by 28% anionic polymer a dosage of 35.7 g/ton was required for travertine suspension while to reach the same settling rate by 34% anionic polymer the required dosage was 47 g/ton for marble suspension. It may be related to the particle size (or particle concentration). Since the particle concentration in marble suspension or the total surface area of marble powders is relatively greater than that of travertine suspension, the required flocculant dosage to reach 1500 mm/min of settling rate for marble suspension would increase. In addition, the travertine is more soluble in water than marble due to relatively higher Mg content of travertine (Table 1). It has been pointed out that the solubility of calcite increases twofold due to inclusion of Mg^{2+} ion in their crystal structure (Kitamura, 2001). In addition, the conductivity measurements of the NSS versus their solid ratio support this inference; that is, the increase in the conductivity of travertine suspension by increasing the solid percent is more than that in the marble suspension (data not given). Hence, it is envisaged that a reduction in the particle concentration of travertine suspension should lower the required dosage for 1500 mm/min of settling rate. As known from the earlier studies on flocculation of different suspension the required dosage to obtain maximum floc size (or maximum settling rate) increases with increase of particle concentration (Yarar, 2001; Swift et al., 2004).

High suspension pH (i.e., pH 11) may affect the flocculation of NSS in two ways: (i) Increases the long range electrostatic or electrical double layer (EDL) repulsive forces between NS particles and Na-PA due to increase in the zeta potential of NS particles (Fig. 1). Therefore, Na-PA-particle attachment can become difficult and this may affects the flocculation negatively. (ii) Leads to more expanded position of polymer chain in suspension enhancing the flocculating power of the polymer and this may affects the flocculation positively. As seen in Fig. 3A and B, until 34% anionic charge, the positive effect of high pH predominates in NSS; in other words, high pH has a net positive effect on NSS flocculation and also enhances settling rate. But in the presence of the highly charged anionic polymer like 40% anionic polymer, this positive effect of high pH is reversed to negative due to sufficiently high EDL repulsive forces between the NS particles of high zeta potential and the polymer of high anionicity degree. Pefferkorn (1999) pointed out that the amount of polymer adsorbed at equilibrium was found to depend strongly on pH for the polyacrylamide/synthetic alumina system and also determined that the amount adsorbed for 15% anionic polymer (hydrolyzed polyacrylamide) is higher than that of 24% anionic polymer at pH 6, while at pH 3 the amount adsorbed for 24% anionic polymer is higher than that of 15% anionic polymer. In addition, Taylor et al. (2002) determined that the overall amount of anionic polymer, which is a HMW polyacrylic acid, adsorbed at pH 8.5 is significantly less (~3 times) than that at pH 4.5 due to electrostatic repulsion between the polymer and the kaolinite. However, as seen in Fig. 3A and B, there is no significant difference between the settling rates at pH values 6 and 7.5. This may result from small difference between pH values. The results indicate that all the polymers except 40% anionic polymer are more effective at basic conditions, i.e., pH 11 than neutral and weak acid medium to flocculate the marble and the travertine suspensions.

3.3. Turbidity

Fig. 4 A and B shows the turbidity values of the supernatant liquid as a function of polymer dosage in the presence of each type of polymer for travertine and marble suspensions, respectively. The turbidity decreases with an increase of polymer dosage to a certain dosage, further increase in the dosage leads to an increase in turbidity again owing to the redispersion of flocculated colloidal particles. Redispersion of colloidal NS particles at high polymer dosage results from the excess polymer adsorption at which the polymer bridging mechanism is prevented. Because there is insufficient free particle surface for

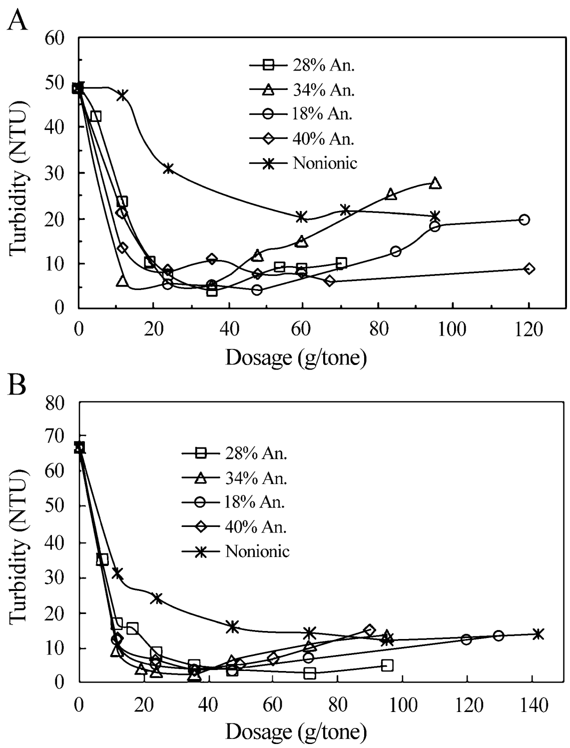


Fig. 4. Turbidity of the supernatant liquid of travertine (A) and marble (B) suspension versus the flocculant's dosage which have different anionic charge at pH 7.5 (natural pH of the suspensions).

bridging contacts to occur and the adsorbed layers may also cause steric repulsion (Gregory, 1989). Indeed, the curves in Fig. 4A and B are the typical examples for flocculation of different suspension systems by HMW anionic, cationic or nonionic polymers (Werneke, 1979; Fan et al., 2000; Yarar, 2001; Divakaran and Pillai, 2002). At low dosages, 34% anionic polymer gave the lowest turbidity (the highest clarity) for both the NSS, while at high dosages, 40% anionic polymer shows the best result for marble suspension (Fig. 4B). By nonionic polymer, the worst (higher turbidity) results have been obtained for marble and travertine suspension at all dosages. This is attributed to inefficiency of nonionic polymer to induce polymer bridging mechanism due to its coiled position in the suspension which affects the flocculation adversely (Stutzman and Siffert, 1977, Yarar, 2001). It is clear from the Fig. 4A and B that in terms of turbidity both marble and travertine suspensions gave similar results almost for each type of polymer; only the effectiveness of the nonionic polymer is relatively better in marble suspension than that in travertine.

Turbidity results from inadequate destabilization of submicron (or colloidal sized) NS particles. It is known that HMW polymers (>10^6) are not generally effective for destabilization but play a very important role in floc development; hence, they are used commonly as flocculants (Hogg, 2000). Here it must be noted that surprisingly, for either travertine or marble suspension, the best results have been obtained by the same polymers if both parameters (settling rate and turbidity) are taken into account. For instance, 34% anionic polymer shows the best performance for settling rate (Fig. 2B) and the supernatant clarity (Fig. 4B) for marble suspension. In general, it is difficult to obtain the best result by the same polymer for both parameters (Werneke, 1979). Therefore, an appropriate flocculant is selected considering the priority of one of the parameters. Furthermore, the minimum turbidity is expected by relatively low charged anionic polymer (i.e., 18 anionic polymer). Since, it is well known that the zeta potential of fine particles is higher than that of large particles due to larger EDL thickness of fine particles (Hunter, 1988). Thus, the colloidal NS particles causing the turbidity have higher zeta potential than the large particles; consequently, it should be expected that the repulsive forces become more important between the colloidal sized particles and the anionic polymer of relatively high anionicity degree. However, this could not be seen in Fig. 4A and B and no explanation could be afforded at this point.

Fig. 5A and B shows the effects of suspension pH on the turbidity of the supernatant liquid of travertine and marble suspension, respectively, after their flocculation by 35.7 g/ton of constant polymer dosage. It is clearly seen that pH 6 and natural pH (pH 7.5) gave the best performance for all the polymers, while pH 11 gave the maximum turbidity by all the polymers for the two suspensions. This may be attributed to destabilization effect of H^+ at low pH and stabilization effect of OH ions at high pH on the negatively charged NS particles. Since, in addition to Ca^{2+}, CO_3^{2-} and HCO_3^-, H^+ and OH^- ions can be considered as potential determining ions for these type NS particles as in the case of calcite mineral (Somasundaran and Ananthapadmananabhan, 1979). In addition, at weak acidic or neutral pH the zeta potential of colloidal marble and travertine particles are in the aggregation (or coagulation) limits (−15 to

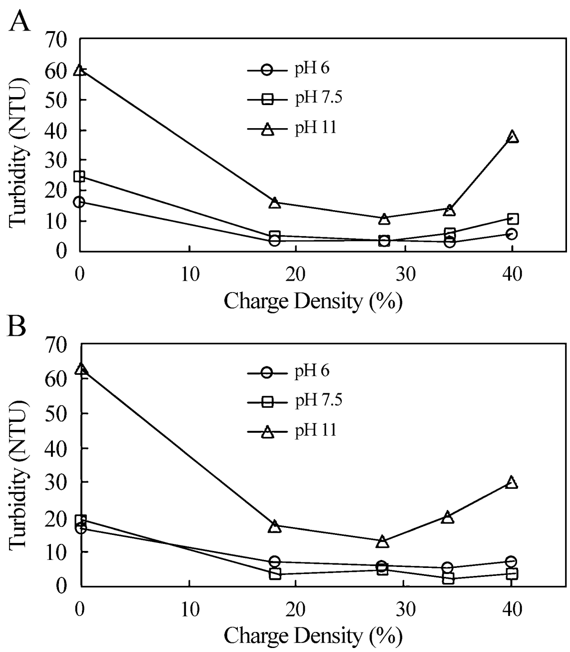


Fig. 5. The influence of suspension pH on the turbidity of the supernatant liquid of travertine (A) and marble (B) suspension at constant flocculant's dosage (35.7 g/ton).

+15 mV), while at pH 11 their zeta potentials are in the dispersion limits (>±15 mV) (Riddick, 1968) as seen in Fig. 1. Therefore, at low suspension pH, the NS particles of colloidal sized may be coagulated prior to flocculation and thus the turbidity in the supernatant liquid decreases. In addition, as seen in Fig. 5A and B, the negative effect of high pH on the turbidity is at minimum level for 18%, 28% and 34% charge density anionic polymers with regard to nonionic and 40% anionic polymers. The 28% and 34% anionic polymers were found suitable in terms of the settling rate and turbidity for travertine and marble suspension, respectively. Since the turbidity values are in the acceptable limits in recycled water used in NS factories, high pH values like pH 11 can be selected as appropriate suspension pH for flocculation of marble and travertine suspensions.

4. Conclusions

The following results can be inferred from this study:

- The polymer charge density and the suspension pH play a crucial role on the flocculation of NSS.
- The type of natural stones has important effect on their settling rate, but the same effect was not observed on their supernatant turbidity.
- The zeta potential curves of NS powders are very different from calcite mineral; that is, isoelectrical point for neither marble nor travertine was not obtained while the calcite exhibits an isoelectrical point at about pH 11 as expected. The electrostatic forces play an important role on polymer–marble and polymer–travertine attachment and thus on the flocculation of NSS.
- In marble suspension, 34% anionic polymer gave the best flocculation performance for both settling rate and turbidity. In travertine suspension, 28% anionic polymer gave the best settling rate, while 34% anionic polymer gave the best clarity at low dosages.
- High suspension pH enhances the settling rate of both the NSS and increases their supernatant turbidity. Since the turbidities are at acceptable levels, pH 11 and 28% anionic polymer for flocculation of travertine suspension, and pH 11 and 34% anionic polymer for flocculation of marble suspension can be selected.

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