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THE EFFECT OF ZETA POTENTIAL ON THE SEDIMENTATION BEHAVIOR OF NATURAL STONE PROCESSING EFFLUENT

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Abstract: One of the main problems for the natural stone industry is treatment of huge amount of waste sludge resulting from the cutting and polishing of them to produce slabs or tiles. The effective treatment of this sludge is very important for reducing of the sludge volume and overall operating costs. Previous studies showed that settling rate and water clarity of the supernatant solution can be increased by flocculation process. In this study, detailed electrokinetic studies were performed on the travertine samples received as natural and slurry form. The natural form of the sample was supplied from a travertine quarry while the slurry was taken from the cutting and polishing process wastewater collector pool of the processing plant. The electrokinetic measurements were conducted to find out the effect of suspension pH and the solid content on the surface potential of solid particles show that zeta potential (ζ) of travertine is positive at pH 9.76 over the all solid contents studied in this work. However, ζ of the particles become negative at lower pH values for 1% solid weight content. In contrast, for travertine slurry (6.73% solid weight), different potential variations were determined. The particles were negatively charged between pH 6 and 8. The results highlighted the effect of dissolved specific ions in the waste slurry and sensitivity of ζ to the ionic strength of the solution. The ζ measurements for a raw travertine sample, performed with different amounts of NaCl additions into the solutions, confirmed the above findings. An addition of low amounts of NaCl decreases ζ of the solid surface. Finally, the ζ measurements in the presence of polymer concentration of 0.001% to 0.1 % (wt/vol) clearly indicated that the flocculant molecules are adsorbed extensively on the travertine particles, and increase the surface potential of the particles with increasing reagent concentration.

***Keywords**: travertine, environment, stone industry, zeta potential*

Introduction

The natural stone industry is one of the oldest in the world. The history of natural stone usage goes back to the ancient time. In fact, two of the Seven Wonders of the Ancient World were built by using Turkish natural stone (Çelik and Sabah 2008). In

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recent years, although much of the international attention in the natural stone industry has been centered on China and India, Turkey is still an important player in the market with a capable of producing over 5 million m^3 of natural stone block. The color and texture qualities compared to other producers and higher travertine reserves provide many advantages to Turkey in the world travertine market. Especially, the Denizli travertine is a very special natural stone mined in limited number of countries in the world (Çobanoğlu and Çelik 2012; Barutçu 2008).

Nowadays, one of the main problems for the natural stone industry in Turkey is the treatment of huge amount of waste sludge resulting from the cutting and polishing of them to produce slabs or tiles. The presence of fine particles in recycled water due to inefficient solid–liquid separation of waste sludge causes several problems. An effective treatment of the sludge is very important for reducing the sludge volume, obtained water quality and overall operating costs. Previous studies concerned the sedimentation of fine particles in waste effluents, for both travertine and marble, showed that settling rate and water clarity of supernatant solution can be increased by using anionic polyelectrolytes. The efficiency of the flocculation process is strongly affected by flocculation pH and the anionic degree of polymers (Bayraktar et al. 1996; Seyrankaya et al. 2000; Arslan et al. 2005; Ersoy et al. 2009). In a recent study performed by Taşdemir and Kurama, (2012), it was confirmed that the solid content, particle size and flocculation polymer type are effective parameters in settling of the suspended particles. However, it was reported that the origin of the slurry and chemical composition of natural stones, especially travertine samples, strongly affect the sign and magnitude of surface potential, and hence sedimentation rate of the solid particle present in the effluents. Therefore, in this study, detailed electrokinetic studies were performed on travertine samples in natural and slurry form. The development of surface charge was discussed taking into account dissolved species, solid content, suspension pH and polymer concentration.

Material and method

Material

Raw and travertine slurry samples used in this study were supplied by Nasip Marble Company (Denizli, Turkey). The natural form of the sample (NT) was supplied from a travertine quarry while the slurry was taken from the cutting and polishing process wastewaters collector pool of the processing plant. The tile and slab production capacity of the processing plant is 250.000 m^2 per year. The Denizli basin is an important region not only in Turkey but also in the world. In the early 1980s, Denizli had only a few quarries, but today the city became an important travertine production and marketing place with approximately 82 travertine and marble processing plants. These plants process a variety of travertine and marbles supplied from their quarries.

The raw travertine sample was firstly crushed and ground in a porcelain ball mill in order to decrease its size for electrokinetic measurements. The chemical composition, determined by the X-Ray fluorescence (XRF), and the physical properties of representative sample is given in Table 1. As can be seen from Table 1, the raw sample mainly consists of $CaCO_3$ with a little amount of MgO, SiO_2 and Fe_2O_3.

The solid content of the slurry was determined by filtering the sample through blue band filter paper. The separated solid was then dried in an oven at 100 °C and weighted to calculate the solid weight %. The solid weight content and the turbidity of the slurry were determined as 6.73% solid weight and >2000 NTU, respectively. The particle size distribution analysis of the particles present in slurry was performed using a Malvern Mastersizer 2000. It was found that 50% of particles were smaller than 40 μm.

Table 1. Chemical and physical analysis results of travertine

Component	%	Property	
MgO	0.56	Specific bulk density, g/cm^3	2.339
SiO_2	0.32	Specific gravity, g/cm^3	2.73
SO_3	0.28	Porosity, %	0.28
CaO	55.00	Water absorption, %	5.51
Fe_2O_3	0.17	Surface area-(BET), m^2 g^{-1}	3.22
LOI	43.67		

Experimental procedures

Electrokinetic measurements of the samples were performed by the electrophoretic method using Zetasizer Nano ZS (Malvern Inst, UK). In each measurement, the suspension was prepared by placing predetermined amount of solid sample, 1, 3, 5, and 10% solid weight, into the 100 cm^3 beaker or for slurry sample, a 50 cm^3 of suspension was placed on a magnetic stirrer, stirred for 10 min and kept for 2 min to allow the coarser particles to settle. Then, 2 cm^3 of solution was taken from the upper part of the beaker, transferred to a closed measurement cell and the zeta potential (ζ) was measured.

In flocculation measurements anionic polymer SPP510 of high molecular weight was used as flocculant. A 1 dm^3 portion of the flocculant stock solution was prepared with distilled water and pre-determined amounts were added to the sample solutions.

Results and discussion

Solubility and gravity settling of travertine particles in waste slurry

The term travertine generally means carbonate rocks (limestone) deposited by supersaturated alkaline mineral waters. Calcium carbonate is poorly soluble in pure water, however, if the pH of the solution decreases, solubility increases due to the increasing carbonic acid concentration in the solution (Lide, 2005).

$$CaCO_3\,(s) \leftrightarrow Ca^{2+}(aq) + CO_3^{-2}(aq) \qquad Ksp = 5.10^{-9} \tag{1}$$

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \tag{2}$$

$$CaCO_3 + H_2CO_3 \leftrightarrow Ca^{2+} + 2\,HCO_3^{-}. \tag{3}$$

The solubility test performed with a supernatant consisting of 5 to 15% solid showed that Ca^{2+} and Mg^{2+} ion concentrations of solutions slightly increase with increasing solid content and contact time, however, in general, it can be concluded that the concentrations of calcium and magnesium ions are independent of the solids content.

The movement of the sludge zone as a function of settling time is given in Figure 1. It was found that sedimentation of fine particles in waste slurry completed within 10 min of setting time. Although the sedimentation process is considered as rapid, the turbidity measurement of the upward water zone shows that it still contains suspended particles, 455 NTU.

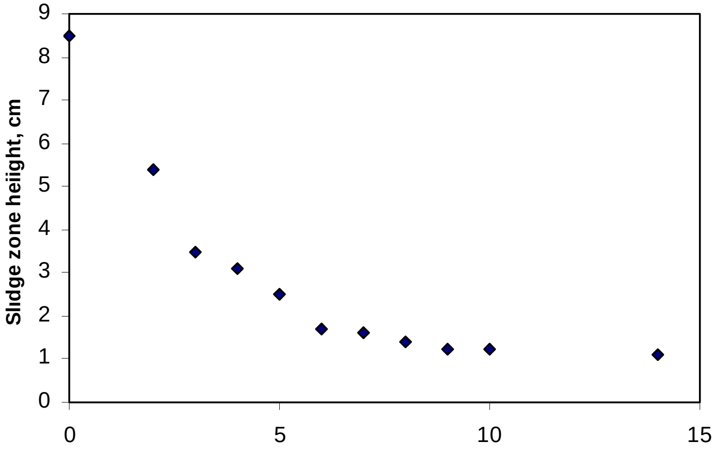

Fig. 1. Gravity settling of travertine particles in waste slurry as function of settling time

Electrokinetic measurements

The effect of the solid content and the pH variation of the solution on ζ potential of the raw travertine sample are given in Fig. 2 and Fig. 3, respectively. It was found that the ζ potential of travertine particles is positive over the whole solid contents range at pH 9.76. The values of ζ potential increase, with increasing solid content from 2.64 mV, to 7.62 mV (for 5% solid weight). A further increase in solids content, resulted in a slight decrease of ζ potential. This could be attributed a small variation of the equilibrium condition of $CaCO_3$ in water with increased solid content.

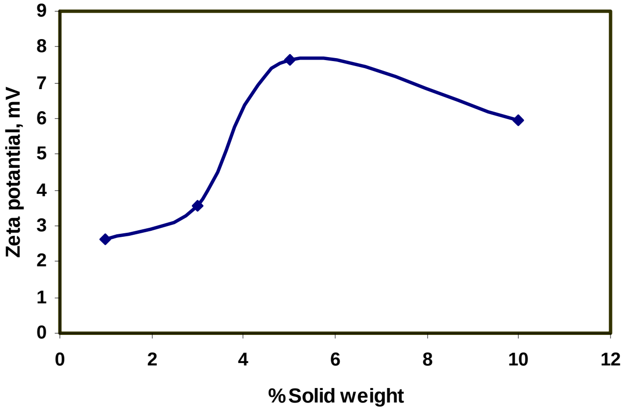

Fig. 2. Zeta potential variation of travertine sample against to solid percent at pH 9.76

The electrokinetic behavior of the $CaCO_3$-water system has been widely studied in literature. It was pointed out that the dissolution of $CaCO_3$ in water (Eq. 1) is affected by small difference in equilibrium condition, modification of solution pH and the hydrolyzing reactions of the dissolved ions. These effects cause variations of both sign and magnitude of ζ potential according to the possible reactions which can be given as follows

$$CO_3^{2-}\,(aq) + H_2O \leftrightarrow HCO_3^-\,(aq) + OH^-\,(aq) \qquad K = 10^{-3.7} \tag{4}$$

$$Ca^{2+}\,(aq) + H_2O \leftrightarrow Ca(OH)^+\,(ag) + H^+\,(aq) \qquad K = 10^{-12.9} \tag{5}$$

$$Ca^{2+}\,(aq) + HCO_3^-\,(ag) \leftrightarrow CaHCO_3^+\,(aq) \qquad K = 10^{1.1}. \tag{6}$$

The Ca^{2+}, CO_3^{2-} and hydrated or hydroxylated species of these ions, such as HCO_3^-, $Ca(OH)^+$, and $CaHCO_3^+$ are considered the major potential determined ions (PDI) while H^+ and OH^- ions are secondary PDI and act as a regulator of concentration of particular anions (Eriksson et al., 2007). Except the above parameters, the measurement methods also play an important role in determine the ζ potential of surface. Recently, Moulin and Roques (2003) reviewed previous findings obtained by different researchers and concluded that the sign of the measured ζ potential is positive, negative, or variable, depending on the measurement conditions, contribution of solubility products, hydrolyzing reactions and availability of foreign ions.

The electrokinetic results given in Fig. 3 indicated that ζ potential of travertine particles have two isoelectrical points (IEP) and the potential values changed between –3 to +3 mV as a function of the solution pH. The ζ potentials slightly move to lower potentials (as negative) with increasing OH^- concentration of the solution. It is approaching the second IEP at about pH 9.4 and than further increase with solution pH leading to positively charged surface.

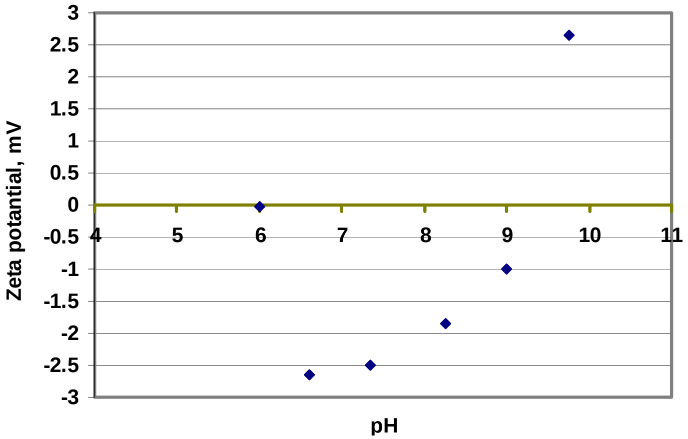

Fig. 3. Variation of zeta potential of travertine sample against solution pH at a solid content of 1%

The decrease of negative potential with increases of pH may be attributed to the possible reaction given below. With increasing pH the surface charge becomes more negative and ζ potential has to decrease. The positive sign can be due to the adsorption of protons. However, we should consider the contribution of foreign cations and anions or organic impurities adsorbed on the particle surface generally observed for natural travertine and calcite samples.

$$CO_3H^-_{surface} + H^+ \leftrightarrow CO_3H^{+2}_{surface} \quad \text{(Moulin and Roques, 2003)} \qquad (7)$$

The previous study performed by Vdovic (2000) dealing with the electrokinetic behavior of both natural and synthetic forms of calcite showed that synthetic calcite has positive ζ potential at pH of pH_{IEP} 8.4, which decreases with either the increase or decrease of pH. Natural calcite, in contrast, has negative ζ potential throughout the investigated pH range of 6–10.

On the other hand, a slight decrease of the negative ζ potential of surface at lower pH values can be attributed to the adsorption of the hydrated carbonate ions in the electric double layer which are closer to the surface of the mineral (inner the Helmholz layer), while calcium ions remain in the outer layer as previously reported by Siffert and Fimbel (1984). When the dispersed mass of $CaCO_3$ in solution is increased, the surface contact with the water phase becomes sufficiently large to ensure rapid equilibrium. Under this condition, certain surface Ca^{2+} cations hydrate until the equilibrium in solution is attained. The surface Ca^{2+} ions are smaller than CO_3^{2-} ions and impart a positive charge to the surface. If dissolution process is still in progress, the absolute values of ζ potential could be a consequence of non-simultaneous detachment of the constituent ions from the surface. Higher loss of $CaOH^+$ than CO_3H^- during dissolution of calcite could explain more negative surface when the system has not yet reached the equilibrium (Stipp and Hochella, 1991).

Rather than the above conclusions, the effect of shrinkage of solid particle and the diminution of the surface on the potential variations with dissolution process, especially lower amount of sample is used, could also be concerned. Calcite or travertine grains in contact with water tend to reach the equilibrium by releasing a certain amount of their constituent ions in the solution. If a smaller quantity of sample is used or if the pH decreases than the IEP, the dissolution will cause a diminution of grains, and consequently the diminution of the available surface area, and ζ- potential of the surface becomes more negative (Moulin and Roques, 2003) .

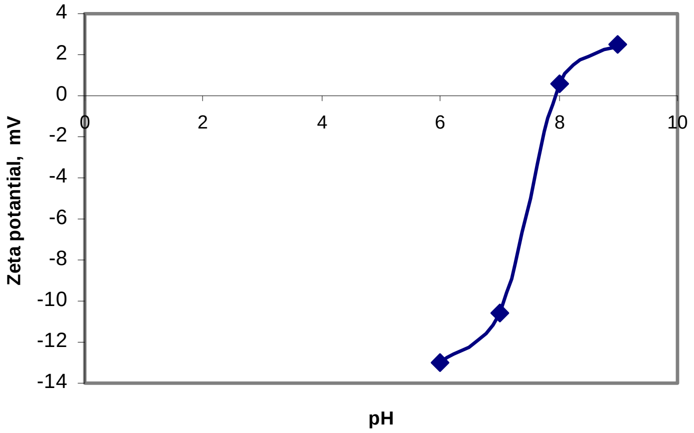

Fig. 4. Variation of zeta potential of travertine slurry as a function of solution pH

Figure 4 shows that the *ζ* potential profile of the solid particles present in the travertine slurry. Differently from the above findings, the particle surface is negatively charged even at lower pH values. This could be attributed to higher concentrations of dissolved specific ions and organic impurities that are found in the waste slurry. The surface properties of travertine are expected to be same as $CaCO_3$. However, greater porous structure and adsorbed or detached organic and inorganic impurities on the surface make it completely different from the solid form (Vdovic and Kralj, 2000).

In order to examine the effect of these ions on surface potential, the ζ-potential measurements were also performed with different amounts of NaCl additions in measurement solutions (Fig. 5). The result confirmed the *ζ* potential of the particle is sensitive to the ionic strength of the solution. In general, *ζ* potential of the surface increases with increasing NaCl concentration. However, compared to electrolyte-free solution, addition of a lower amount of NaCl to the solution decreases ζ potential of particles. For 0.002 M NaCl addition, ζ-potential of the solid surface decreases from 2.64 mV to -1.34 mV.

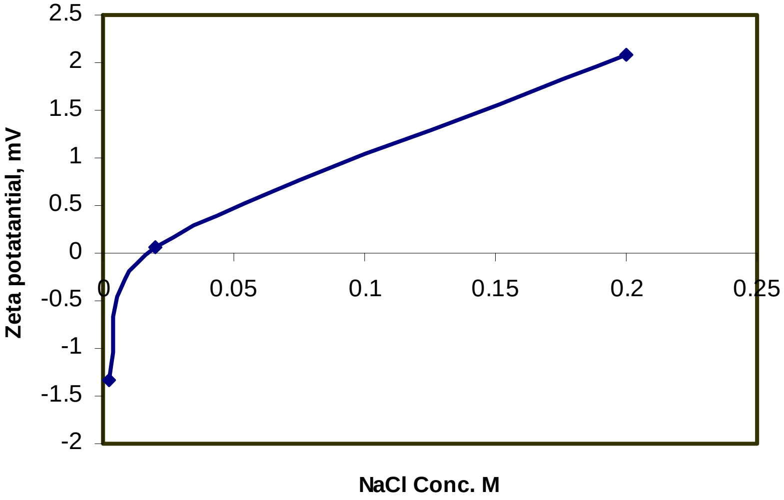

Fig. 5. Zeta potential variation of 1% solid content suspension as a function of NaCl concentrations at pH 9–10

The positive values measured above 0.1 M NaCl addition may be attributed to the ion-ion interactions and ion-surface interactions of the structure-making cations and structure breaking anions or foreign ions that are present in the solution and the difficulties of measuring ζ potential above 0.1 mol dm^{-3}. As previously discussed by Kosmulski and Rosenholm (1996), the electric field around a colloidal particle could hardly be measured at electrolyte concentrations above 0.1 mol dm^{-3} using traditional equipment. At low ionic strengths, the electrolytes of alkali halides (1-1) show common properties. The isoelectric point of oxides and many other solids does not depend on the nature and concentration of these salts. However, for the electrolytes involving multivalent ions, in contrast, the isoelectric points are shifted. The direction and magnitude of the shift depends on the nature and concentration of the electrolyte. At higher ionic strengths, far fewer water molecules per ion are available, and due to this water deficit, some ions experience partial dehydration. This dehydration allows the ions to approach closer to the surface. Moreover, the hydration shell is distorted and finally the individual properties of particular ions and salts are displayed in ion-ion interactions or in ion-surface interactions that are not important under lower ionic strength conditions. When the ionic strength exceeds a critical value, which is below 0.1-mol dm^{-3} for common 1-1 salts, the iep starts to shift gradually toward higher pH values with increasing ionic strength. Finally, when the ionic strength exceeds a second critical value, there is no iep and the ζ potentials are positive over the entire measured pH range.

Kosmulski et al. (2003) studied the electrokinetic potentials of mineral oxides and calcium carbonate in artificial seawater, and released a relatively same conclusion. It was reported that ζ potentials of concerned materials are depressed in the presence of a high salt concentration. In case of calcium carbonate, measured ζ potential equal to 1.91 mV by electroacoustic method at pH 8 in artificial seawater (at high ionic strengths) is substantially lower than the previously published results at low ionic strengths. Within the studied pH range of 7–9, calcium carbonates showed pH independent ζ potentials potential.

The variation of zeta potentials as a function of polymer concentration for flocculation process is given at Fig. 6.

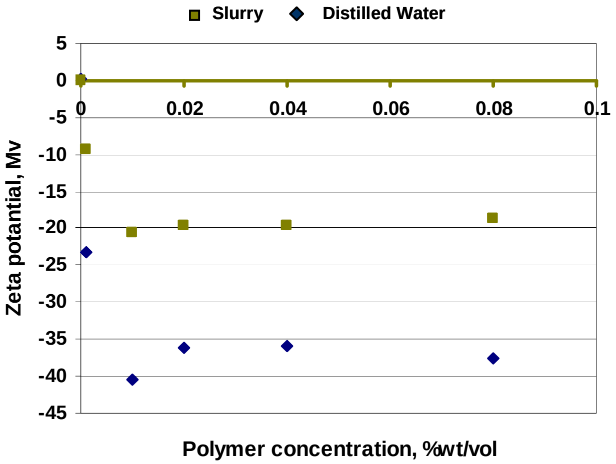

Fig. 6. Zeta potential variation of 1% solid content travertine suspension as a function of polymer concentrations (0.001%–0.08% wt/vol). pH 8–8.5

It is clearly indicated that the flocculant molecules adsorbed extensively on the travertine particles, and lower amount of reactive addition is sufficient to increase the surface potential of the particles to fall into the stabile region. ζ potential of the particle surface sharply increases from –8.4 mV to –36.7 mV for the solution consisting of 1% with polymer addition of 0.05% wt/ vol. and a further increase of the flocculant concentration does not cause any considerable effect on the ζ potential values. In the case of the slurry sample, this increase is negative (from 0.6 mV to –16 mV).

This conclusion can be supported by the results from the previous paper in which ζ potential of calcite in the presence of organic acids was investigated. Positive surface charge of calcite was reduced by introduction of fulvic acid to the solution. The high affinity of fulvic acid molecules for calcium carbonate surface is due to electrostatic attraction between positively charged surface sites and the negative charge (Vdovic and Kralj, 2000).

For the coagulation or coagulation + flocculation aid sedimentation processes the measurement of ζ potential is accepted as an effective tool for coagulation control because the changes in zeta potential indicate changes in the repulsive force between colloids. The magnitude of zeta potential gives an indication of the potential stability of the colloidal system. If all the particles in suspension have a large negative or positive zeta potential then they will tend to repel each other and there will be no tendency for the particles to come together. On the other hand, if the particles have low zeta potential values, then there will be no force to prevent the particles coming together and coagulation. Therefore, the first step for effective coagulation is the destabilization of the suspension by eliminating these repulsive forces. Either compressing the double layer through pH control or addition of electrolytes can overcome the energy barrier between particles. Double layer compression involves adding salts to the system. As the ionic concentration increases, the double layer and the repulsion energy curves are compressed until there is no longer an energy barrier. Particle agglomeration occurs rapidly under these conditions because the colloids can just about fall into the van der Waals "trap" without having to surmount an energy barrier (Somasundaran and Das, 1998, www.zeta-meter.com). In practice, a large amount of electrolyte addition alone is an impractical technique for water treatment. However, usage of dual flocculant or coagulation + flocculation can help to increase flocculation efficiency. As discussed previously, although the solubility of the travertine particles in suspension is very low, a relatively high concentration of Ca^{2+} and Mg^{2+} ions in waste slurry, 360.72 mg Ca^{2+} /dm^3 and 340 48 mg Mg^{2+} /dm^3 at pH of 7.75, leads to decreasing ζ potential of particles and approaching the surface charge the isoelectric point (Fig. 4). The availability of such ions in solution improves the binding of the anionic polymer segments onto the negatively charged surface (Hiemenz and Rajagopalan, 1997). Such ions act as "bridges-with bridges" to induce flocculation.

Conclusion

According to the experimental finding discussed above, the following conclusion can be drawn. The electrochemical measurement results showed that the surface charges of the travertine particles in distilled water are strongly affected by the suspension pH and the solid content of solution. It was found that the surface potential of solid particles is positive at pH 9.76 over the all solid contents studied. However, ζ potential of the particles becomes slightly negative values at lower pH values for 1% solid weight content. For travertine slurry, different potential variations were determined. The particle surfaces are negatively charged between pH values of 6 and 8 due to the higher concentrations of dissolved specific ions i.e. Ca^{2+} and Mg^{2+} in the waste slurry. These results highlight the importance of influence of the source of the slurries on the surface charge or the magnitude of potential of particles and confirmed that ζ potential of the particle surface is sensitive to the ionic strength of the solution. Furthermore, it can also propound that availability of such ions in the solution allows the elimination of repulsive forces between particles and destabilizes the suspension to effective adsorption of polymer molecules to each particle.

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