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Effects of physical variables on settling velocities of calcium and strontium phosphates in mother solution

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ABSTRACT: Settling velocity is an important parameter used in modeling solid-liquid flow operations and for evaluating tank volumes in water treatment technology. In the present study, series of bench-scale batch-wise precipitation and settling tests were performed to evaluate the effect of some physical variables such as precipitate concentration, temperature and stirring on settling velocity of tricalcium diphosphate (TCDP) and tristrontium diphosphate (TSDP) in mother solution. Various amounts of TCDP and TSDP precipitates were generated in reaction mixtures, by mixing sub-saturated equi-molar solutions (0.1M) of the respective ions in various metal to phosphate (M/P) volume ratios (10:90ml; 20:80ml; 30:70ml; 40:60ml; 50:50ml; 60:40ml; 70:30ml; 80:20ml; 90:10ml). Settling velocity diagrams of TCDP and TSDP were obtained as functions of M/P volume ratio, temperature, and repeat stirring. The results showed that whereas temperature and stirring variables had a linear relationship with precipitate settling velocity, a non-linear relationship was observed between the precipitate concentration variable and settling velocity. When the temperature of the mixtures were raised from 30^{o}C to 50^{o}C, 0.76- and 0.45- fold increases in settling rate were recorded for TCDP and TSDP, respectively. On the other hand, with repeated stirring of TSDP precipitate, 83% increase in settling velocity was recorded between the first and third stirrings. The results may be employed in settling tank designs for the removal of phosphates in water treatment process. ©JASEM

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Keywords: settling velocity, mother solution, batch-wise precipitation, temperature, amount of precipitates, $Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$.

Settling velocity, which is the residence time taken for particles in suspension to settle under gravity, is used in modeling solid-liquid flow operations and is one of the most important parameters used in evaluating tank volumes in wastewater treatment technology.

Several mathematical models have been proposed which provide empirical and theoretical descriptions of settling data. One of such is the Vesilind's power law equation (equation1), which describes a decreasing function of settling velocity with increasing particle concentration (Zhang, *et al.*, 2015; Vander Hasseltand Vanrolledhem, 2000) as

$$V_g = V_0 exp^{-nX} \quad (1)$$

where V_g - settling velocity; X - solid concentration; V_0 - maximum settling velocity and n - settling index.

Although, the models do not provide description for physiochemical processes such as precipitation (Kazadi-Mbamba *et al.*, 2015), they describe settling data from physical processes only. Obunwo and Iboroma, (2015) had reported that solid phase particles, produced from liquid medium, settle under gravity as sediments. Both the formation and settling of these precipitates can be influenced by physical and chemical variables including temperature (Victor, *et al.*, 2007), concentration of reactants (Obunwo *et al.*, 2014), concentration of precipitates (Mekhamer, *et al.*, 2013) as well as border conditions such as size of vessel (Obunwo *et al.*, 2014) and pH. In continuation of the study on sedimentation (Obunwo and Iboroma, 2015), the effect of precipitate concentration, temperature and stirring variables on settling characteristics of tricalcium diphosphate and tristrontium diphosphate in their mother solutions have been investigated, by employing a batch-wise 'Simultaneous Ions Variation Method'. The objective is to provide settling velocity data of tricalcium diphosphate and tristrontium diphosphate which hitherto have not been provided. Data may be employed in sedimentation tank designs for removal of phosphates in water treatment process.

MATERIALS AND METHODS

Analar grade $CaCl_2$, $SrCl_2.6H_2O$, and Na_3PO_4 from BDH Chemicals Limited, Poole, England, were used. Others materials included 100ml cylinder, digital stopwatch, thermometer, and a thermostated water-bath with model number XMTD-204. The salts were weighed on a Gulfex Medical and Scientific electronic weighing balance and the solutions were prepared with de-ionized water. A bench-scale settling apparatus (settleometer) was set-up using the 100ml cylinder (with a transparent measuring tape affixed), a stirrer and a digital camera.

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Precipitation and Measurement of settling velocities: Insoluble phosphates of Calcium and strontium were produced by mixing aqueous solutions of their salts. The experimental procedure used in this study was a modification of the initial rate method (Obunwo, *et. al.*, 2014), to describe a Simultaneous Ions Variation Method. Settling tests were performed on various amounts of precipitates generated batch-wise in reaction mixtures. To achieve this, sub-saturated solutions (0.1M) of $CaCl_2$, $SrCl_2$, and Na_3PO_4 were prepared by weighing out and dissolving 11.098g, 26.662g, and 16.394g, respectively in 1000ml of de-ionized water. 10ml of $CaCl_2$ or $SrCl_2$ was mixed with 90ml of Na_3PO_4 solution to form $Ca_3(PO_4)$ or $Sr_3(PO_4)$ precipitate. The precipitate was stirred for 120 seconds before it was allowed to settle. The cylinder was bench-mounted and provided with a diffuse lighting behind (3.1 watts LED rechargeable desk lamp) to enhance illumination(Obunwo&Iboroma,2015). The digital camera was also bench mounted and set to capture images of the suspension front every 60 seconds. The procedure was repeated at 20:80ml; 30:70ml; 40:60ml; 50:50ml; 60:40ml; 70:30ml; 80:20ml and 90:10ml metal ions to phosphate ions volume ratios. These volume combinations were coded 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 in mole fraction terms, to represent the reagents mixing or volume ratios and the degree of particle saturation that were generated upon mixing at 30^{o}C. In all the experiments, monitoring and recording processes were terminated between the 15th and 22nd minute when compression settling was minimal.

In the investigation of the effect of stirring on the precipitates residence time, two volume-ratio combinations were selected (one from each) based on interface clarity. For strontium phosphate, the 20:80ml volume ratio, was selected. The precipitate formed was stirred for 120 seconds and allowed to stand. After about 22 minutes of settling, the settled particles were re-suspended homogeneously by stirring for another 120 seconds. Again, after another 22 minutes the precipitates was re-suspended and settling process monitored as before. Similarly, 30ml of 0.1M Ca^{2+} and 70ml of 0.1M PO_4^{3-} which gave 30:70ml (0.3) volume ratio was used for $Ca_3(PO_4)_2$. The experiments were carried out in the thermostated water-bath set at 30^{o}C.

In the investigation of the effect of temperature, the 30:70ml volume ratio was selected for both the calcium and strontium and settling tests were performed in the thermo stated-water bath set at 30, 35, 40, 45, and 50^{o}C.

RESULTS AND DISCUSSION

Formation of calcium or strontium phosphate precipitates: The solid-phase tricalcium diphosphate (TCDP), $Ca_3(PO_4)_2$ and tristrontium diphosphate (TSDP), $Sr_3(PO_4)_2$, particles were formed by the simplified stoichiometric chemical reactions illustrated in equations 1 and 2.

$$3CaCl_{2(aq.)} + 2Na_3PO_{4(aq.)} \rightarrow Ca_3(PO_4)_{2(s)} + 6NaCL_{\ (aq.)} \quad (2)$$

$$3SrCl_{2(aq.)} + 2Na_3PO_{4\ (aq.)} \rightarrow Sr_3(PO_4)_{2(s)} + 6NaCL_{\ (aq.)} (3)$$

The 10:90ml and 90:10ml M/P ratios which represent 0.1 and 0.9 (volume) mole fractions did not yield much precipitate. This was made evident by the appearance of a white less-dense gelatinous suspension. The presence of a clear supernatant and suspension boundary were indicative of high particle distribution and low precipitate solubility, which in real systems would enhance complete removal or recovery of either calcium or strontium phosphate. It was further observed that the precipitate saturation that occurred upon mixing increased as the mixing ratio approaches the stoichiometric equivalence and then decreased thereafter. The greatest particle saturation was observed at 50:50ml and 60:40ml M/P volume ratios. However, settling rate data of TSDP precipitate at 90:10ml volume ratio was not recorded due to absence of a clear suspension zone.

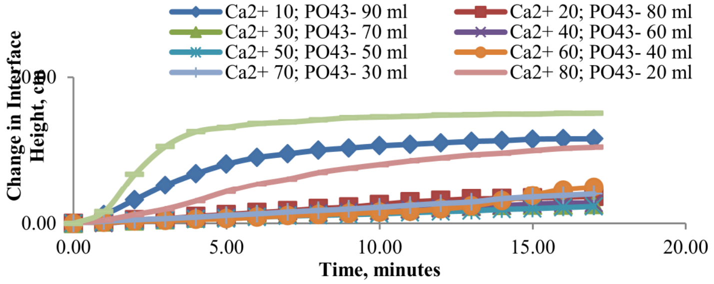
Effect of Precipitate Concentration on initial settling velocity:Figures 1A and B illustrate the settleability tests results of TCDP and TSDP precipitates at 30^{o}C. Initial settling velocities of the precipitates were also evaluated from the slopes of change in interface height against time, at the linear portions, with regression fit of $r^2 > 0.97$. Figure 2 illustrates data of evaluated initial settling velocities against M/P volume ratio. The results show that settling characteristics of TCDP and TSDP precipitates vary with precipitate concentration. The variation is however non-linear as may be seen in Figure 2. The following order in initial settling velocity (in M/P mixing ratios) may be written for TCDP and TSDP precipitates:

TCDP:
90:10ml≫10:90ml≫80:20ml>20:80ml>70:30ml
>40:60ml>30:70ml>60:40ml>50:50ml.

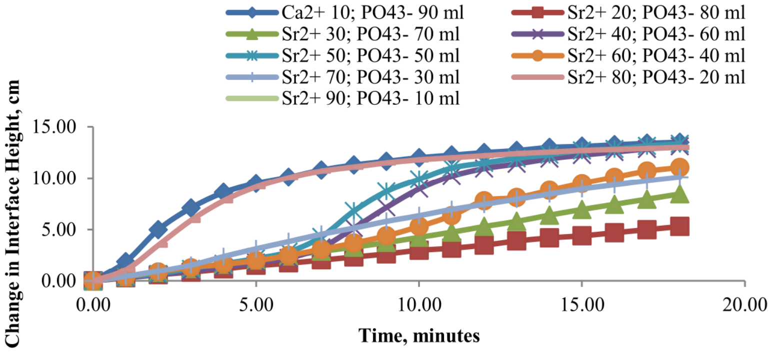
TSDP:
10:90ml≈80:20ml≫70:30ml>50:50ml>60:40ml
≈30:70ml≈40:60ml>20:80ml.

Based on the batch-wise precipitation (Kirboga and Oner, 2013) procedure adopted, similarity in settling characteristics of precipitates and particles in conventional hindered settling mode was assumed. Consequently, results were analyzed using Vesilind's power law model of gravitational sedimentation (equation 1). Strong and weak negatively correlated settling indexes with $0.65 \leq r^2 \geq 0.28$ were obtained (figure not given) for TCDP and TSDP, respectively.This suggests that, though disperse phase content is the most important physical parameter that affect viscosity (Nutan and Reddy, 2010), chemical interactions of particles with the aqueous chemical environment (Obunwo *et al.*, 2014) may have considerable effects on initial particle stability in the medium. In an aqueous environment, interactions due to surface adsorptions and solution-driven interaction of precipitates with H^+ and OH^-(Recillas *et al.*, 2012; Bouchoud *et al.*, 2010) affect settling behaviours.

1A



1B



Figure

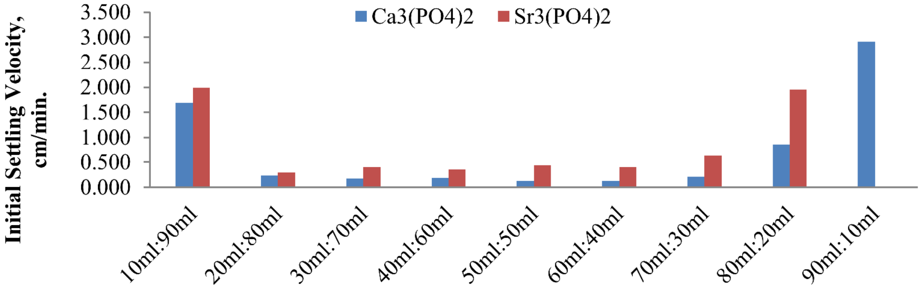


Fig 2: Effect of M/P (volume) ratio on precipitate initial settling velocity.

Effects of Stirring Variable: Results of TCDP and TSDP precipitates settling behaviours monitored in three consecutive stirrings are plotted in Figures 3A and B. As may be seen, a 0.83-fold increase in initial settling rate occurred when TSDP suspension was stirred the third time in the 35th minute. However, TCDP was not much affect as illustrated in Figure 3A, suggesting that it has a stable structure at that composition and temperature. TSDP precipitate, on the other hand might have changed from a more colloidal state to crystalline one in the process of controlled stirring and longer induction time which enhanced its rapid settling.

Effect of temperature variable: Results of TCDP and TSDP initial settling velocities measured in various temperatures are plotted in Figure 4. It can be seen that when the temperature was raised from 30°C to 50°C settling rate increased by 76% for $Ca_3(PO_4)_2$ and 45% for $Sr_3(PO_4)_2$. These findings imply that the scaling or deposition tendencies of these compounds will be high at higher plant temperatures in industrial water treatment systems. Figure 4 also illustrate the difference in density between the two substances, TSDP being denser than TCDP has a higher settling rate at all temperatures.

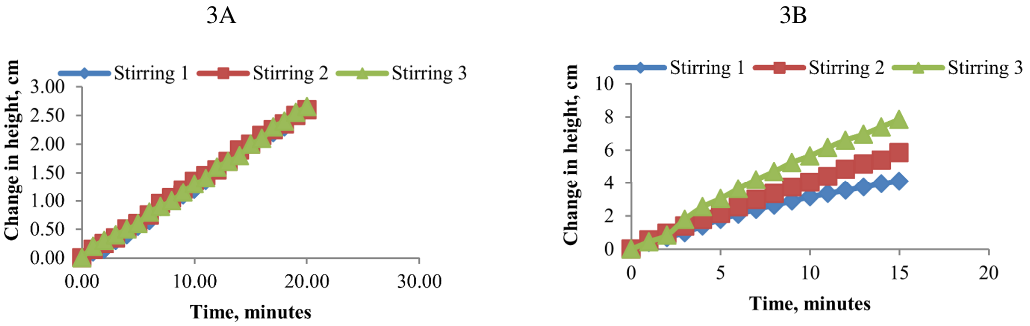


Fig 3: Residence time taken for (A) TCDP and (B) TSDP precipitates, at 30:70ml and 20:80ml (M/P) volume ratios.

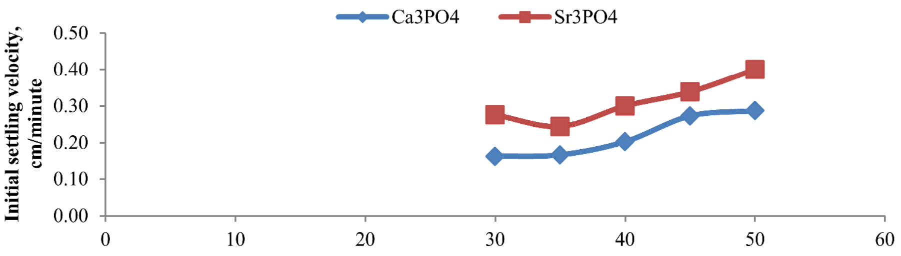


Fig 4: Initial settling velocity against temperature for TCDP and TSDP.

Conclusion: This study has captured the dependence of some physical variables – concentration, temperature and stirring – on the settling velocities of TCDP and TSDP precipitates. Whereas temperature and stirring have linear relationship with settling velocity, a non-linear relationship exists with precipitate concentration. The study has also provided data of settling velocities of the precipitates which were hitherto not available. These data may be employed in the construction of sedimentation tanks for the removal of phosphates in water treatment process.

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