Separation of phosphoric acid sludge: effect of flocculation on settling and P₂O₅ recovery rates

Rim Jouraiphy [1], Islaam Anouar [2], Hamid Mazouz [3], Jihane Mendil [4], Amina Ibnlfassi [1]

[1] Engineering, Industrial Management, and Innovation Laboratory, Faculty of Science and Techniques, University Hassan I, BP: 577, Settat, Morocco

[2] Laboratory of Analytical Chemistry and Physico-Chemistry of Materials, Department of Chemistry, Faculty of Sciences Ben M'Sik, Hassan II University Av Driss El Harti B.P 795, Casablanca, Morocco

[3] OCP. SA Jorf Lasfar, El Jadida Morocco

[4] CBS laboratory, University Mohammed VI Polytechnic, Lot 660, Hay Moulay Rachid 43150, Benguerir, Morocco

Corresponding author: h.mazouz@ocpgroup.ma (Hamid Mazouz)

Abstract: Phosphoric acid sludge is one of the prominent problems in the phosphate industry. Its formation is co-occurred by considerable losses of P₂O₅ that affect the process performance. Management and valorization of this waste is a key issue. This work aimed to deal with this industrial concern by studying the influence of the flocculation on the sludge sedimentation and thus the P₂O₅ recovery rate. The flocculation tests were conducted in the presence of various types of anionic polymers. The effect of dosage, molecular weight, and type of flocculant were examined. The results indicated that all polymers showed settling performance improvement. And, the flocculant with the highest molecular weight (*F1*), showed the best settling performance with a pace of 3.3 cm/min and the lowest turbidity value of 40.4 NTU using a dosage of 5 ppm. Due to its high molecular weight, this polymer carries a polyelectrolyte bridging mechanism, which allows the absorbed polymer to move further away from the surface of the particle and then increases the particle radius, the number of collisions, and thus the particle size. However, for the P₂O₅ recovery rate, the sulfonic polymer (*F5*) was the best performer allowing recovery of 78.8% of the total mass of the sludge. *F5* is weakly amphoteric. Polymers containing sulfonic acid groups are known to be inherently powerful than the carboxylic acid groups as they are stable due to their high energy barrier. According to the results, the flocculation increases the recovery of P₂O₅, which represents a profit of more than 30 kg of clarified phosphoric acid per 1 tone of sludge.

Keywords: phosphoric acid sludge, flocculation, P₂O₅ recovery rate, dosage, molecular weight

1. Introduction

Phosphoric acid is the most produced acid in the world after sulfuric acid (Mecibah et al., 2012). It is a necessary raw material for various processes, especially for phosphate-based fertilizers. The production of phosphoric acid, by the wet process, is carried out by the reaction of phosphate rock with a mineral acid, mainly the sulfuric acid, according to Reaction 1 (Becker, 1989):

$$Ca_3(PO_4)_2 + 3H_2SO_4 + 6H_2O \rightarrow 3(CaSO_4 \cdot 2H_2O) + 2H_3PO_4 \qquad (1)$$
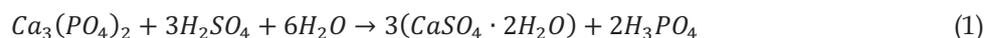
The above reaction results in the production of phosphogypsum (*PG*), as solid waste and weak phosphoric acid 27-29% P₂O₅. The latter is concentrated to reach 50-54% P₂O₅, commercial-grade, using a forced circulation evaporation process (Becker, 1989). During this step, saturated solid, due to water removal by evaporation, leads to the formation of phosphoric acid sludge (*PAS*) after desupersaturation and decantation steps (Gilmour, 2014).

PAS management has attracted much attention from production engineers and researchers in the phosphate industries. It has a direct impact on production performance, promoting the P₂O₅ recovery,

as one of the performance indicators of phosphoric acid production. The complexity of *PAS* management is related to its characteristics as a muddy, slushy mass, and sediment (Allen and Berry, 1981). Thus, the most used management technique in the phosphate industries is gravitational settling, using tanks, to recover the acid estimated at more than 60% of the total mass of the sludge (Becker, 1989). However, the inadequacy of this technique results in the presence of fine particles in the recovered acid, which causes settling issues during the phosphoric acid separation and transport. Moreover, decanted sludge always has a high acid content, which represents a loss of more than 1% in phosphoric acid production (Fayard et al. 1983; Becker, 1989).

Particles in solutions carry charges on their surface, leading to suspension stabilization. These charges prevent particles from coming together and retards settlement by keeping the particles in constant motion (Zahrim et al., 2019). The addition of substances leads to change the surface property of colloidal particles and to precipitate them (Tripathy and Ranjan, 2016). In this field, the flocculation is the commonly used technique. It occurs when the contact between the particles is augmented, allowing the formation of aggregates or flocs by agglomerating dispersed particles (Wber, 1972; Lee et al., 2012; Basaran and Tasdemir, 2014).

Many types of polymeric flocculants are commonly used in the flocculation process: cationic, anionic, and non-ionic, facilitating the recovery either of the solid or the liquid part (Lee et al., 2012; Basaran and Tasdemir, 2014). These polymers have dual functions: neutralize charges of the colloidal particles and bridge the aggregated destabilized particles together to form flocs (Chong, 2012). Flocculation rate and efficiency depend on several factors related to the flocculant such as the type, the molecular weight (M_W), the structure of the polymer, and the charge density of the flocculant or the solution like the mineralogical composition, the particle size, the pH, and the chemical composition of solutions (Ipekoglu, 1997; Somasundaran and Das, 1998; Hocking et al., 1999; Besra et al., 2000; Sworka et al., 2000; Yarar, 2001; Cengiz et al., 2004; Ersoy, 2005; Gergory, 2006; Henderson and Wheatley, 2007; Cengiz et al., 2009; Gregory and Barany, 2011; Tasdemir et al., 2011; Chong, 2012; Tasdemir and Kurama, 2012; Tasdemir and Tasdemir, 2012, Basaran and Tasdemir, 2014; Tripathy and Ranjan, 2016).

The flocculation is a currently used technique in the solid-liquid separation processes. In the industry of phosphoric acid, the flocculation is used to improve acid filtration. Generally, the flocculants utilized are anionic polyelectrolytes, such as polyacrylamides (Kaesler et al., 1989; Irwin, 2012; Allaedini and Zhang, 2018). In the literature, many studies have been conducted to investigate the enhancing of phosphoric acid and *PG* separation by filtration using flocculation (Kaesler et al., 1989; Irwin, 2012; Davis et al., 2015; Wiatr, 2019). These studies reported that high M_W of anionic polymers were commonly used. Yet, few researchers were conducted to determine the *PAS* flocculation. Allaedini and Zhang (2018), in their study on the effect of sonication on sludge flocculation and the settling rate, used the flocculation of the *PAS*. The study concluded that the sonication prepared the slurry for enhanced interaction between the flocculant and the slurry, resulting in enhanced sludge settlement. Although direct flocculation generates less volume of sludge because the flocs formed with strong bridging mechanisms are denser and closely packed (Lee et al., 2014). A recent study of the same authors investigated the effect of polymeric flocculant properties on filtration and recovery of rare-earth elements from phosphoric acid sludge. The study explored further the correlations between M_W and sludge settling rate (Allaedini and Zhang, 2019). Nevertheless, there has been no researches studying the effect of dosage, M_W, and type of flocculant on the P_2O_5 recovery from *PAS*.

This work was aimed to study the flocculation effect on enhancing the settling and P_2O_5 recovery rates of *PAS*. The clarification effect of the resulting phosphoric acid from flocculation was studied using several types of flocculants by varying the M_W and the dosage. The flocculation performance was also characterized by measuring the settling and P_2O_5 recovery rates as well as the optimal dosage of polymer and the residual turbidity.

2. Materials and methods

2.1. Materials

2.1.1. *PAS* sludge sample

The *PAS* sludge (Fig. 1) used in this study was collected from the 54% P_2O_5 phosphoric acid decanter in the phosphoric acid production unit of OCP Jorf Lasfar, Morocco, where the concentrated acid was

settled. The particle size distribution of the sample was determined using Malvern Mastersizer 2000, United Kingdom, and the results are shown in Fig. 2. As seen in Fig. 2, the particle sizes were under 400 µm with 50% being under 35.01 µm. The volume average of the *PAS* was 51.612 µm. It was determined that D_{10}, D_{20}, D_{50}, and D_{90} of the solid particles by volume were 7.37 µm, 11.89 µm, 35.01 µm, and 113.12 µm, respectively.

To detect the minerals in the PAS sample, the X-Ray Diffraction *(XRD)* analysis the solid phase of the sample was made using Bruker AXS D-8 diffractometer (Cu-Ka radiation in Bragg–Brentano geometry, q–2q). For this purpose, the minerals were separated from the PAS sample by centrifugation at a speed of 3500 rpm for 15 min. The solid phase obtained was washed two times with distilled water and one time with a mixture of water (2/3) and acetone 99.8% (1/3), provided from *Pure Chem*, to eliminate the phosphoric acid trace and the organic matter from the mineral surfaces. Finally, the solid was recovered by the centrifugation at a speed of 3500 rpm for 15 min, dried, and then analyzed using the *XRD* (Fig. 3). The *XRD* results of the sample confirmed that the particles of phosphoric acid sludge were predominately composed of the Gypsum $CaSO_4$, $2H_2O$, the Malladrite Na_2SiF_6 Sodium as a minor element, the Anhydrite $Ca(SO_4)$ that precipitates during concentration of the acid and the Chukhrovite $Ca_4Al_2(SO_4)F_{12}(H_2O)_{12}$.

Fig. 1. Phosphoric acid sludge (*PAS*)
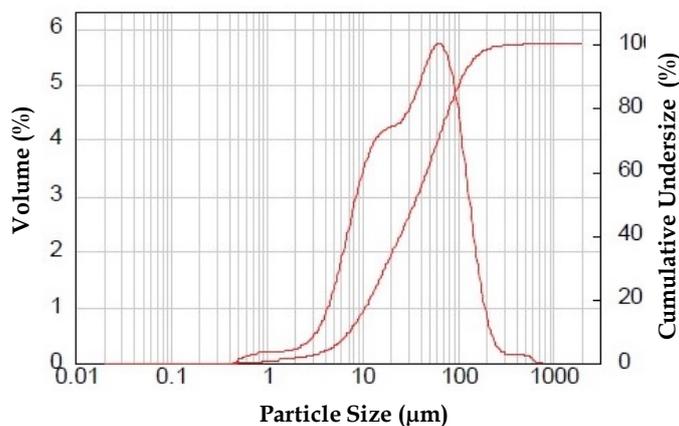
Fig. 2. Particle size distribution of the *PAS* sludge

The P_2O_5 analysis of the sludge was measured using a method based on *UV* spectroscopy using the UNICO SQ2800 UV/VIS Spectrophotometer. The technique consists of forming a vanadium phosphomolybdate complex by the reaction of orthophosphate ions with an acid solution containing molybdate and vanadate ions. The orthophosphate ions were obtained after the digestion of sludge samples with a perchloric acid at high temperatures. The absorbance of the solutions complex was measured using UV spectroscopy to determine the P_2O_5 concentration. The physical characterization of the raw *PAS* solid is presented in Table 1.

Additionally, the zeta potential measurements of the particles in the *PAS* sludge were carried out using the Malvern Nano-Z model. The measurements were conducted at a 0.1% solids ratio with a solid refraction index of 1.531 and an adsorption of 0.1. The zeta potential of the minerals in the *PAS* sample

was found at a pH of -0.32 as + 12.8 mV (Table 1). The stability of the particles in the acid was low, and the particle charge was positive. The pH and the conductivity of *PAS* were measured using the Multimeter HANNA HI 2211 pH/ORP Meter, and the turbidity was measured using the Turbidimeter HACH 2100Qis (Table 2).
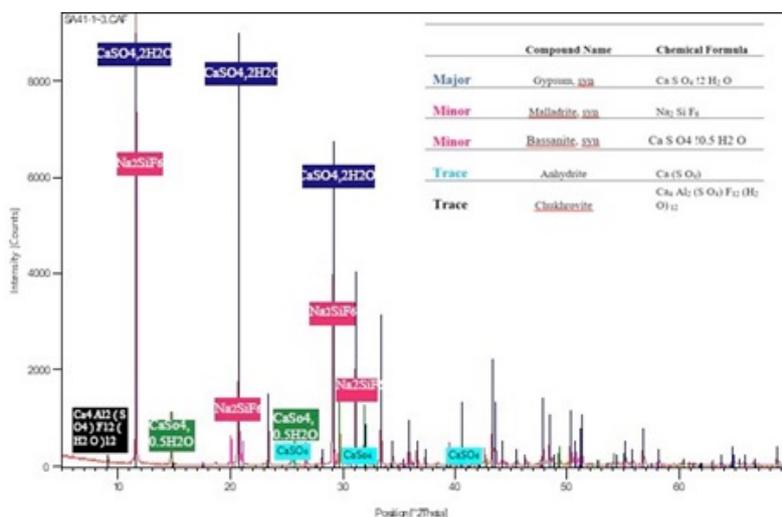
Fig. 3. *XRD* analysis for the solid in the *PAS* sludge

Table 1. Physical characterization of the *PAS* sludge

Sludge sample	Temperature	pH	P_2O_5 concentration	Density	Viscosity (40°)	Solid content	Zeta potential (mV)
Well Mixed	40°C	-0.32	56%	1.9	27 CP	28%	+12

Table 2. pH, conductivity, and turbidity of *PAS* and the supernatant acid

pH		Conductivity (mS/cm)		Turbidity (NTU)	
Sludge	Supernatant acid	Sludge	Supernatant acid	Sludge*	Supernatant acid
-0.32	-0.29	66	81.3	-	92.66

*With a solid content of 28%, the turbidity of the sludge cannot be measured

2.1.2. Flocculants

The flocculation experiments for the *PAS* sludge were carried out using five polymers with different molecular weight (M_W) and the same density charge. Solid anionic flocculants were selected as a derivative of the polyacrylamide with high M_W in the form of dry polymer. Scanning electron microscopy (*SEM*) and Energy Dispersive X-ray spectroscopy (*EDX*) analyses were conducted to identify the composition of the polymers. Figure 4 shows the *SEM-EDX* analysis of the shape and composition of the solid flocculants as received and before the preparation. The results showed that *F1* and *F2* were characterized by small spherical particles, unlike *F3*, *F4*, and *F5*, with larger particles and irregular shapes. The shape of the flocculant can influence its dissolution. Regarding the composition, *F1*, which was a sulfonic flocculant, included in its composition various elements such as fluorine, magnesium, aluminum, sodium, and phosphorus. While fluorine, aluminum, and magnesium improve the thermal insulation, lower the critical surface tension, and enhance the dielectric characteristics. Furthermore, sodium in a polymer allows retaining water during the dissolution. The flocculants with a carboxyl group, *F2*, *F3*, *F4*, and *F5*, had almost the same composition (amides). The presence of molybdenum and thallium in *F3* strengthens its heat and light stabilization and reduces its coefficient of friction.

The choice of flocculants was based on three criteria: The flocculant composition and M_W, and the pH of the sludge. Chosen flocculants are effective in acidic solutions. The flocculants previously

mentioned were evaluated. Based on the literature, the additives were diluted at a concentration of 1 g/dm^3 in water by adding 0.5 g of each flocculant to 500 g of demineralized water and stirred for 3 hours. The turbidity, the refractive index, the density, and the miscibility time were noted for each solution. The measurements were conducted using, respectively, the Turbidimeter *HACH 2100Qis,* the Refractometer *Abbe ORT-1,* the Densimeter *Mettler Toledo™ 51324450,* and the Chronometer. Turbidity, refractive index, density, and miscibility time of the flocculant solutions (1 g/dm^3) were noted. The characteristics of each flocculant are given in Table 3.

Table 3. Dissolution characteristics of the flocculants

Flocculant	Flocculant type	Molecular weight	Turbidity	Refractive index	Density	Miscibility time (min)
F1	Carboxyl	13 M	2.21	1.3341	0.997	254
F2	Carboxyl	10 M	1.89	1.3339	0.994	160
F3	Carboxyl	11 M	2.08	1.3340	0.996	185
F4	Carboxyl	15 M	2.35	1.3338	0.995	212
F5	Sulfonic	12 M	1.76	1.3324	0.992	84

Miscibility is associated with the type of flocculant, the flocculants containing carbon chains are known to have a lower solubility in aqueous media (Tarleton and Wakeman, 2007). The dissolution of the flocculant particles in aqueous solution is of great importance in the flocculation process. It allows in one hand the activation of the chemical agent of the polymer and on the other hand accurate its mobility and capacity to attain solid particles (Greville, 1997). The dissolution parameter determines the degree of compatibility of two polymers or one polymer and one solvent (Hansen, 2007). Several properties govern the miscibility of flocculant particles in water such as a degree of polymerization, the radius of gyration, and the structure factor (Lindving et al., 2002). At this level of research, studying the flocculants dissolution according to these parameters needs further studies and calculations. Thus, the dissolution was studied by comparing the turbidity, the refractive index, the density, and the miscibility time values. These parameters, describing the cloudiness of a fluid and the degree of compactness of a substance, give enough information about the dissolution.

Based on the three characteristics: The results for turbidity, refractive index, and density of the flocculants showed that for the five flocculants, the values were close. This was due to the existed correlation between the refractive index and the other parameters such as density (Castillo et al., 2010). However, the miscibility time of the flocculant varied between 84 min and 254 min. The flocculant presenting the best conditions of dissolution was *F5* as its particles dissolved in 72 sec once in contact with the water.

2.2.   Methods

2.2.1.   Flocculation experiments

2.2.2.   Flocculant dosage

As the flocculation can be affected by dosing and mixing conditions, the flocculation tests were carried out to evaluate the required dosage to achieve optimum particle capture. In this study, the flocculation behavior of *PAS* was determined by applying classical jar tests according to the Standard Practice for Coagulation-Flocculation Jar Test of Water *ASTM D 2035*. The tests were performed in the presence of five different types of polymers at different dosages. Three specific consummations: 5, 7, and 10 ppm per ton of PAS were evaluated according to the usual consumption of phosphate industry. For all tests performed, 1000 g sludge was heated at 40°C to simulate the operating conditions in the plant. Before the flocculant addition, the sludge was mixed at 70 rpm for 3 min. The flocculant was quickly added in the vortex using a syringe to allow a high dispersion. The duration of mixing for each test was 2 min. The samples were let settled down for 5 h, and the supernatant acid was recovered. The turbidity of the recovered acid was measured to choose the optimal dosage. For incertitude identification, the tests were repeated four times.

2.2.3. Settling rate

Following the same conditions of dosage tests, the flocculation was achieved using the Jar test by adding the optimal dosage at the same stirring speed. After 2 min of mixing, the *PAS* sample was added to a graduated cylinder with an inner diameter of 50 mm, and a height of 400 mm used for monitoring the flocs settling velocity. The samples were settled down for 8 h. The settling rate was calculated by monitoring the height of the settled solid over time. To interpret the correlation between the floc size and the settling rate, the floc size was measured using *Ceti 1202.5000M Microscope MAX II Trinoculaire* coupled *to Leica DMC2900* camera. For incertitude identification, the tests were repeated four times.

Fig. 4. *SEM- EDX* analysis of the five tested flocculants: (a) *F1*, (b) *F2*, (c) *F3*, (d) *F4*, and (e) *F5*

2.3.   Methods

2.3.1.   Flocculation experiments

2.3.2.   Flocculant dosage

As the flocculation can be affected by dosing and mixing conditions, the flocculation tests were carried out to evaluate the required dosage to achieve optimum particle capture. In this study, the flocculation behavior of *PAS* was determined by applying classical jar tests according to the Standard Practice for Coagulation-Flocculation Jar Test of Water *ASTM D 2035*. The tests were performed in the presence of five different types of polymers at different dosages. Three specific consummations: 5, 7, and 10 ppm per ton of PAS were evaluated according to the usual consumption of phosphate industry. For all tests performed, 1000 g sludge was heated at 40°C to simulate the operating conditions in the plant. Before the flocculant addition, the sludge was mixed at 70 rpm for 3 min. The flocculant was quickly added in the vortex using a syringe to allow a high dispersion. The duration of mixing for each test was 2 min. The samples were let settled down for 5 h, and the supernatant acid was recovered. The turbidity of the recovered acid was measured to choose the optimal dosage. For incertitude identification, the tests were repeated four times.

2.3.3.   Settling rate

Following the same conditions of dosage tests, the flocculation was achieved using the Jar test by adding the optimal dosage at the same stirring speed. After 2 min of mixing, the *PAS* sample was added to a graduated cylinder with an inner diameter of 50 mm, and a height of 400 mm used for monitoring the flocs settling velocity. The samples were settled down for 8 h. The settling rate was calculated by monitoring the height of the settled solid over time. To interpret the correlation between the floc size and the settling rate, the floc size was measured using *Ceti 1202.5000M Microscope MAX II Trinoculaire* coupled *to Leica DMC2900* camera. For incertitude identification, the tests were repeated four times.

2.3.4.   Recovery rate

As the settling profiles cannot give a definitive idea about the most appropriate flocculant, the tests were carried out to evaluate the recovery rate of *PAS* for each flocculant. The recovery rate criterion ($RR_{P_2O_5}$) describes the amount of P$_2$O$_5$ $m_{P_2O_5}(R)$ recovered from the initial amount of P$_2$O$_5$ in the sludge $m_{P_2O_5}(S)$ and therefore the rate of recoverable losses. It is calculated by multiplying the concentration of P$_2$O$_5$ by the mass of the recovered liquid or solid and the solid content of recovered liquid $sc(RL)$ or solid $sc(S)$. Below the recovery rate Eq. (1).

$$RR_{P_2O_5} = \frac{m_{P_2O_5}(R)}{m_{P_2O_5}(S)} = \frac{X_{P_2O_5}(R) \cdot m(RL) \cdot (1 - sc(RL))}{X_{P_2O_5}(S) \cdot m(S) \cdot (1 - sc(S))} \tag{1}$$

The recovery rate was measured by separating the two phases after 8 hours of sedimentation.

3. Results and discussion

3.1. Effect of flocculant dosage on flocculation performance

The tests were carried out at different polymer dosages, varying between 3 and 7 ppm per ton of *PAS*. After 5 h of settling, the turbidity of the recuperated acid was measured to evaluate the clarification effect of the flocculant. Figure 5 shows the effect of flocculant type and dosage on the turbidity for the same physical characteristics of the sludge.

The turbidity of the recuperated acid, after *PAS* settling, was 92.66 NTU. By adding a dosage of 3 ppm, the turbidity decreased for the five flocculants to reach a minimum of 40.4 NTU with *F1*. The increasing of the polymer dosage from 3 ppm to 5 ppm allowed the turbidity decreasing for the four flocculants *F2*, *F5*, *F3*, and *F1* to achieve a minimum of 24.8 NTU. By reaching the dosage of 7 ppm, the turbidity increased. It reached for *F3* a maximum value of turbidity of 70.5 NTU. Nevertheless, for *F4*, the optimal dosage was the 3 ppm that decreased the turbidity from 92.66 to 60.4 NTU. In principle, the substantial degree of flocculation is not necessarily achieved with the highest dosage of the polymer. It clarifies the capacity of the dosage 3 ppm (for *F4*) and 5 ppm (for *F1*, *F2*, *F3*, and *F5*) to decrease the turbidity of the sludge more than 7 ppm. Guibai and Gregory (1991) noticed that for high solid content,

flocculation could increase rapidly with relatively low polymer doses, as theoretically, to reach effective flocculation, only the half surface of the particles must be covered (Hogg, 1992; Basaran and Tasdemir, 2014). In the case of the dosage of 7 ppm, the sensitivity between the incorrect dosages and turbidity is explained by blocking the bridging mechanism of the polymer at the surface of the particles. This is due either to the complete coverage of the particle surface by the absorbed polymer layer and to the excess adsorption of polymer molecules with each other (Tripathy and Ranjan, 2016). Thus, overdosing can be a serious concern. It might generate a well-established suspension extremely hard to separate.
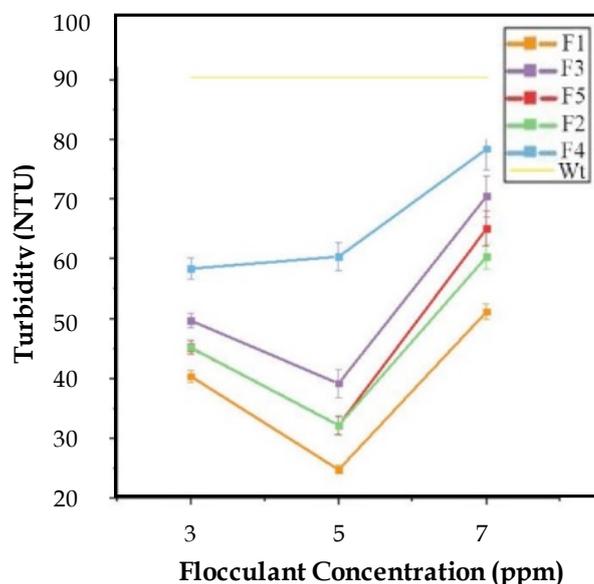
Fig. 5. Turbidity of the recuperated acid after flocculation

3.2. Effect of flocculant molecular weight (M_W) on flocculation performance

The correlation between M_W and sludge settling was identified. In principle, higher M_W results in better activity for the same type of molecule (Pillai, 1997). Though the increasing M_W, in some instances, results in loss of activity, which is the case for the *F4*, having a M_W of 15 M but reaching a minimum of turbidity of 58.4 NTU with a dosage of 3 ppm. This is due to the high viscosity of the higher M_W flocculants that leads to the difficulty of their distribution through the sludge. Moreover, high M_W polymer contains long-chain polymer per unit of weight, as linear structures with two dimensions (Basaran and Tasdemir, 2014). Its solution might not contain enough polymer molecules to flocculate all the solids in high solid content slurries (Tripathy and Ranjan, 2016). Furthermore, it has been observed that beyond an optimal M_W, the flocculation efficiency decreases, which is attributed to steric repulsion between polymer molecules.

Besides, using a low M_W flocculant leads to high consumption of the flocculant as shown by Allaedini and Zhang (2018) using for *PAS* flocculation an anionic flocculant solution with a concentration of 0.07%. The difference is due to the low M_W of the Percol 156 (8-10 M) comparing to our studied flocculant.

3.3. Effect of flocculant type on flocculation performance

By comparing the results in terms of flocculant type, *F1* as a sulfonic polymer showed the best results, followed by *F2*, *F5*, and *F3* containing an important percentage of carboxylic groups than *F4*. Polymers containing sulfonic acid groups are known to be inherently stronger than the carboxylic acid groups due to their high energy barrier. They retain their anionic charge and activity in media with low pH (Tripathy and Ranjan, 2016; Polymer Properties Database, 2020). This type of flocculant serves as filtration aids in the production of phosphoric acid (Kaesler et al., 1989; Irwin, 2012; Davis et al., 2015; Wiatr, 2019). These filtration aids enhance the removal of precipitated calcium sulfate dihydrate (*PG*) from the phosphoric acid (Kaesler et al., 1989; Rey and Hunter, 1994). Furthermore, structured polymers

containing carbon chains need higher optimum doses to improve flocculation (Tarleton and Wakeman, 2007).

In the case of *F4*, the high turbidity can be explained by the absence of the sodium. It forms complexes with sulfate and fluorine, avoiding the presence of particles in the recovered acid. Mottot (2000) showed that the increasing amounts of sodium ions decreased the turbidity of the recuperated liquid.

3.4. Effect of flocculation on *PAS* settling rate

Figure 6 shows the height of the settled solid as a function of the time. The different profiles showed that flocculation significantly improved the decantation of *PAS*. The optimal dose used for *F2*, *F3*, *F5*, and *F1* was 5 ppm and 3 ppm for *F4* at a sludge concentration of 28%. According to Fig. 6, the average pace settling of the *PAS* without flocculation (Wt) was 11.2 cm/min. *F1* showed superior performance with an average of 3.3 cm/min. *F2*, *F3*, and *F5* showed a good performance with almost the same average pace of 5 cm/min. However, *F4* was the least efficient flocculant with a pace average of 7.4 cm/min.
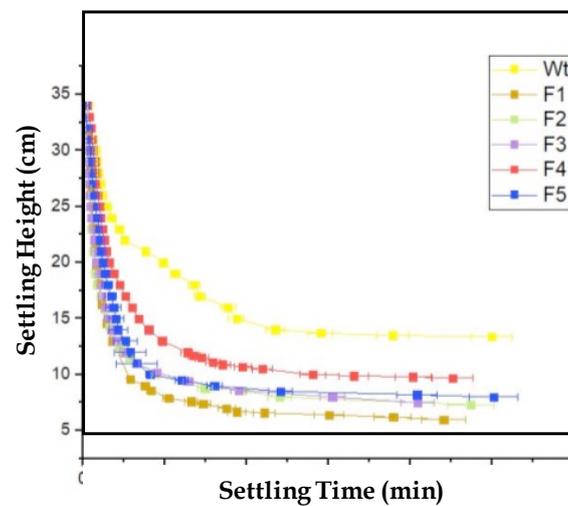
Fig. 6. Settling rate of the *PAS* after flocculation

Settling rate is controlled by particle properties as density, shape, and size and also by fluid properties as density and viscosity (Floyd et al., 2016). In this study, the main criterion to follow was the floc size used in the understanding of aggregation mechanisms. Several studies have shown an affinity between floc sizes and velocity gradients (Matsuo and Unno, 1981; Hopkins and Ducoste, 2003; Sun et al., 2016). The floc size gives an idea about the capacity of the flocculant to form flocs in important size and determines the effectiveness of solid removal processes. The determination of the physical characteristics of flocs can be measured using several techniques such as optical microscopy, automated image analysis system, laser diffraction techniques, and photometric dispersion analyzer. To evaluate the effect of the different flocculants on the settling rate, particle optical microscope images were used to measure the floc size distribution of recuperated solid. Formed flocs by various flocculant showed different floc characteristics affecting the velocity gradient (Shatat et al., 2008).

According to the optical microscope image and visual observations (Fig. 7), *F1* showed the biggest particles followed by *F2*, *F3*, and *F5*. Yet, *F4* showed different particle sizes. As shown by Gill and Herrington (1988) by using polymers with different M_W but the same charge density, floc size increased with increasing the M_W. Two phenomena can define the mechanism of flocculation; bridging and electrostatic patch mechanisms. According to Chen et al. (1992), the floc formed using different M_W carries a polyelectrolyte bridging mechanism with high M_W polymers and a charge neutralization mechanism with low M_W polymers (Chen et al., 1992). As the M_W is decreasing, a gradual transition between the mechanisms is recorded. With the bridging mechanism, the adsorbed polymer can move further away from the surface of the particle. It increases the particle radius, the number of collisions, and thus the particle size (Tripathy and Ranjan, 2016). Usually, for sedimentation as a solid-liquid

separation, high M_W flocculants are preferable since they are related to the bridging mechanism. They are more effective in improving their bridge formation capability for colloidal particles, resulting in a more rapid floc size development, which is beneficial to improve the settling rate (Gao et al., 2002; Wickramasinghe et al., 2002; Shatat et al., 2008). Therefore, in the case of sedimentation, this mechanism is stronger related to other flocculation mechanisms.

During the clarification of the phosphoric acid, the flocculating agent is generally added to produce rapid settling in a reasonable period. During this step, flocculant amounts from about 5 to 15 ppm based on the acid solution are effective. Typically, as shown by Allen and Berry (1981), amounts of about 10 ppm are suitable when employing the Nalco 7873 as flocculating agents. In our study, using anionic high M_W flocculants allowed us to optimize the dosage (5 ppm).
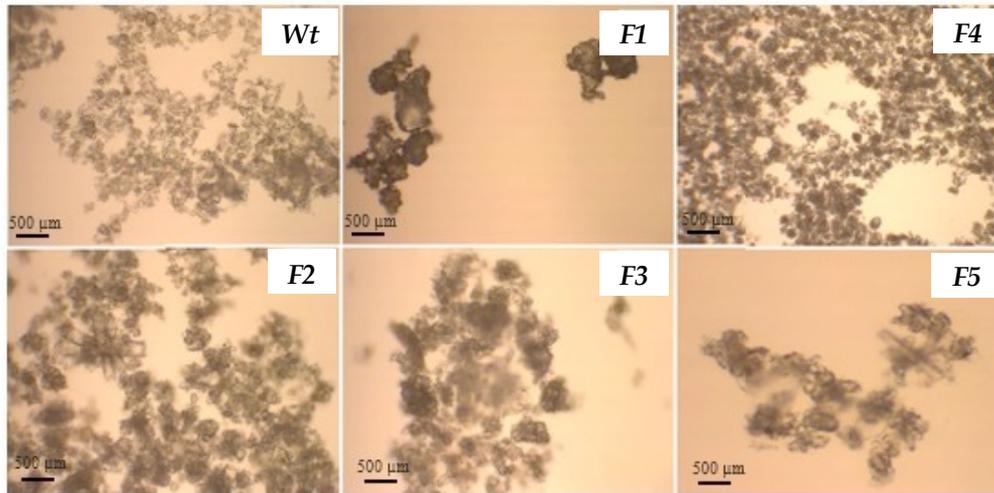
Fig. 7. Optical microscope images of the formed flocs

3.5. Effect of flocculation on P_2O_5 recovery rate

The results of P_2O_5 the recovery rate are showed in Figs. 8 and 9. The flocculant $F5$ gave the best P_2O_5 recovery rate with 78.8% P_2O_5, followed by $F3$, $F1$, $F4$, with respectively 77.7%, 77.2%, and 75.9%. $F2$ gave the same recovery rate as sludge without flocculant addition 75.6%. Contrary to what is expected, the flocculants that allowed the best settling rate are not the ones that allowed the best P_2O_5 recovery rate. For the settling velocity, $F1$ gave the best performance, but for the recovery rate, the $F5$ gave the best performance. The difference between the settling rate and recovery rate is that, in the case of $F1$, the polymer produces a highly agglomerated sludge, but the flocs may produce a wet and soggy cake that can hardly be handled (Novak and Haugan, 1980). In principle, the flocs formed with strong bridging mechanisms are denser and closely packed (Guibai and Gregory, 1991). The reason behind this
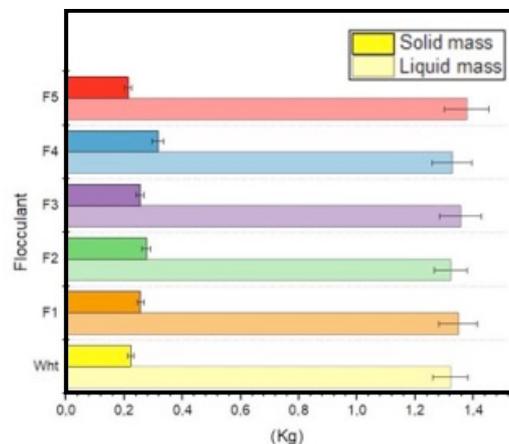
Fig. 8. Solid and liquid mass after the separation
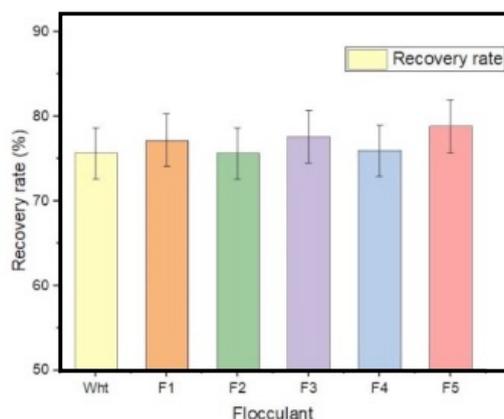
Fig. 9. P_2O_5 recovery rate
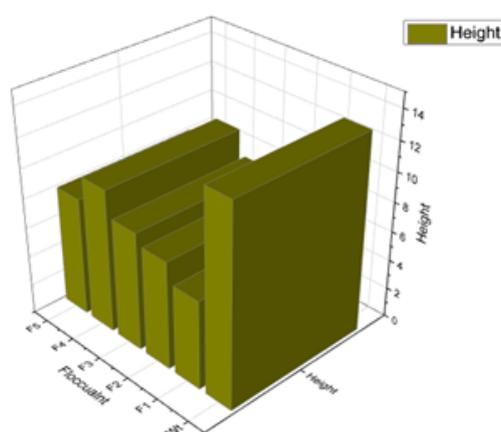
Fig. 10. Height of deposit solid

is that the flocs formed with high M_W products might be relatively large, trapping acid within the structure and increasing the final solid moisture. It can also explain the difference between the heights of the recuperated solid shown in Fig. 10.

4. Conclusions

Flocculation tests were carried out in the presence of five different types of polymers at different dosages. The choice of flocculants was based on three criteria: The composition and the M_W of the flocculant and the pH of the sludge. Flocculation and clarification behavior of *PAS* suspension was studied by determining the residual turbidity values, the settling rate, and the P_2O_5 recovery rate. The condition for the maximum settling rate and the minimum turbidity after settling was observed at optimum flocculant dosage for each flocculant. It was observed that type, M_W, and dosage of the flocculant have an important effect on the settling and P_2O_5 recovery rates. All flocculants used in the tests substantially reduced the turbidity of *PAS* suspensions and improved the settling rate. However, it was determined that in terms of the settling rate and turbidity, the *F1* with a M_W of 13 M showed a better flocculation performance compared to the other flocculants with an average of 3.3 cm/min. The high molecular weight of this flocculant carries a polyelectrolyte bridging mechanism, which allows the absorbed polymer to move further away from the surface of the particle and then increases the particle radius, the number of collisions, and thus the particle size. Nevertheless, in terms of the P_2O_5 recovery rate, *F5* showed the best performance, with 78.8% P_2O_5 recovered. This type of flocculant, as a sulfonic polymer, keeps its activity even in low pH environments. Polymers containing sulfonic acid groups are known to be inherently stronger than the carboxylic acid groups. In this field, it will be interesting to study the effect of dilution of the flocculant with the phosphoric acid instead of water to minimize the addition of water to the phosphoric acid production process and improve the quality of the acid.

References

ALLAEDINI, G., ZHANG, P., 2018. *Treatment of phosphoric acid sludge for rare earths recovery II: Effect of sonication and flocculant solution temperature on settling rate*. Sep. Sci. Technol., 54, 1842-1852.

ALLAEDINI, G., ZHANG, P., 2019. *Treatment of phosphoric acid sludge for rare earths recovery I: Effect of polymeric flocculant properties on filtration and recovery*. IJSEIMS., 7, 1-18.

ALLEN, H.L., BERRY, W.W., 1981. *Purification of phosphoric acid.* United States Patent Office, N°22 083.

BASARAN, H.K., TASDEMIR, T., 2014. *Determination of flocculation characteristics of natural stone powder suspensions in the presence of different polymers*. Physicochem. Probl. Miner. Process., 50(1), 169-184.

BECKER, P., 1989. *Phosphates and phosphoric acid: Raw Materials, technology, and economics of the wet-process.* 2nd ed., Mercel Dekker. New York.

BESRA, L., SENGUPTA, D.K., ROY, S.K., 2000. *Particle characteristics and their influence on dewatering of kaolin, calcite and quartz suspensions.* Int. J. Miner. Process., 59, 89-112.

CASTILLO, J., GUTIERREZ, H., RANAUDO, M., VILLARROEL, O., 2010. *Measurement of the refractive index of crude oil and asphaltene solutions: Onset flocculation determination.* Energ. Fuel., 24, 492-495.

CENGIZ, I., SABAH, E., ERKAN, Z.E., 2004. *A study on the flocculation performances of traditional and UMA technology polymers.* Madencilik, 43, 15-23.

CENGIZ, I., SABAH, E., OZGEN, S., AKYILDIZ, H., 2009. *Flocculation of fine particles in ceramic wastewater using new types of polymeric flocculants.* J. Appl. Polym. Sci., 112, 1258-1264.

CHEN, W., WALKER, S., BERG, J., 1992. *The mechanism of floc formation in protein precipitation by polyelectrolytes*. Chem. Eng. Sci., 47, 1039-1045.

CHONG, M., 2012. *Direct Flocculation Process for Wastewater Treatment, in: S.K. Sharma, R. Sanghi, Advances in Water Treatment and Pollution Prevention.* Springer Netherlands, 201-230.

DAVIS, R.V., MOSS, W.L., STROMINGER, M.G., RENZELLO, R., FAIGL, T.A., HAY, D.N.T., 2015. *Phosphoric acid production gypsum filtration flocculant pre-dilution (make down) with post-filtration phosphoric acid.* United States Patent Office, N° 9 187 327 B2.

ERSOY, B., 2005. *Effect of pH and polymer charge density on settling rate and turbidity of natural stone suspensions.* Int. J. Miner. Process., 75, 207-216.

FAYARD, C., SIBERCHICOT, J.C., CHAMPION, J., SIMONET, A., LATRIE, J.C., 1983. *Process for producing purified phosphoric acid, apparatus and obtained product.* European Patent Office, N° 254 946 A1.

FLOYD, I.E., SMITH, S.J., SCOTT, S.H., BROWN, G.L., 2016. *Flocculation and settling velocity estimates for reservoir sedimentation analysis.* US Army Corps of Engineers.

GAO, B., HAHN, H., HOFFMANN, E., 2002. *Evaluation of aluminum-silicate polymer composite as a coagulant for water treatment.* Wat. Res., 36, 3573-3581.

GERGORY, J., 2006. *Particles in water: Properties and Process*. University College London, UK.

GILL, R., HERRINGTON, T., 1988. *Floc size studies on kaolin suspensions flocculated with cationic polyacrylamides.* Colloid and Surfaces, 32, 331-344.

GILMOUR, R., 2014. Phosphoric acid: *Purification, uses, technology and economics.* CRC PressTaylor & Francis Group, New York.

GREGORY, J., BARANY, S., 2011. *Adsorption and flocculation by polymers and polymer mixtures*. Adv. in Colloid Interface Sci., 169, 1-12.

GREVILLE, A.S., 1997. *How to select a chemical coagulant and flocculant.* Alberta Water & Wastewater Operators Association, 22th Annual Seminar.

GUIBAI, L., GREGORY, J., 1991. *Flocculation and sedimentation of high-turbidity waters*. Wat. Res., 25(9).

HANSEN, C.M., 2007. *Hansen Solubility Parameters: A User's Handbook Second Edition.* CRC Press Taylor & Francis Group, New York.

HENDERSON, J.M., WHEATLEY, A.D., 2007. *Factors affecting the efficient flocculation of tailings by polyacrylamides.* Int. J. Coal. Preparation, 4, 1-49.

HOCKING, M.B., KLIMCHUK, K.A., LOWEN, S., 1999. *Polymeric flocculants and flocculation.* Polymer Reviews, 39(2), 177-203.

HOGG, R., 1992. *Hydrodynamic effects in flocculation and dispersion of fine-particle suspensions.* Plenary lecture presented at Engg. Foundation Conf. On Dispersion Aggregation, Fundamentals and Applications, Palm Coasi, Florida.

HOPKINS, D.C., DUCOSTE, J.J., 2003. *Characterizing flocculation under heterogeneous turbulence*. J. Colloid. Interface. Sci., 264, 184.

IPEKOGLu, U., 1997. *Dewatering and Methods. Dokuz Eylül University,* Mining Faculty Impress, No: 179, Izmir.

IRWIN, L., 2012. *Method for improving gypsum phosphoric acid slurry filtration using carboxymethyl cellulose.* United States Patent Office, Nº 8 182 698 B2.

KAESLER, R.W., ROBINSON, D.G., MOSS, W.L., FAILON, B.K., 1989. *Filtration aids for removal of calcium solids from aqueous phosphoric acid.* United States Patent Office, Nº 4 800 071.

LEE, C.S., ROBINSON, J., CHONG, M.F., 2014. *A review on application of flocculants in wastewater treatment,* Process. Saf. Environ., 6, 489-508.

LEE, K.E., MORAD, N., TENG, T.T., POH, B.T., 2012. *Development, characterization and the application of hybrid materials in coagulation/flocculation of wastewater: A review.* Chem. Eng. J., 203, 370-386.

LINDVIG, T., MICHELSEN, M.L., KONTOGEORGIS, G.M., 2002. *A Flory–Huggins model based on the Hansen solubility parameters.* Elsevier Fluid Phase Equilibria, 203, 247-260.

MATSUO, T., UNNO, H., 1981. *Forces acting on floc and strength of floc.* J. Environ. Eng., ASCE107, 527.

MECIBAH, W., DELIMI, R., GABLI, M., 2012. *Removal of cadmium from phosphoric acid by electrodialysis.* Rev. Sci. Tech. 24, 84-90.

MOTTOT, Y., 2000. *Coagulants et flocculants,* 279th Conference of l'Université de tous les savoirs.

NOVAK, J.T., HAUGAN, B.E., 1980. *Mechanisms and methods for polymer conditioning of activated sludge.* WPCF, 52 (10), 571-2580.

PILLAI, J., 1997. *Flocculants and coagulants: The keys to water and waste management in aggregate production.* Nalco Company, Naperville.

Polymer Properties Database, Polymer Chemistry Online, https://polymerdatabase.com, Accessed 15 March 2020.

REY, P.A., HUNTER, W.E., 1994. *Method of clarifying phosphoric acid using high charge sulfonic polymer.* United States Patent Office, Nº 5 173 280.

SHATAT, R., ARIFFIN, A., NORULAINI, N., RAHMAN, A., ABDUL KADIR, M.O., 2008. *The effect of molecular weight and charge density on floc size distribution of palm oil mill effluent flocculated with cationic polyelectrolytes.* AJBAS 4, 95-103.

SOMASUNDARAN, P., DAS, K.K., 1998. *Flocculation and selective flocculation - An overview.* In: Atak, S., Onal., G., Celik, M.S., Proceedings of 7th International Mineral Processing Symposium (Innovation in mineral and coal processing), Istanbul, Turkey, Balkema, 81–91.

SUN, S., SHIRK, M.W., LION, L.W., 2016. *Characterization of flocs and floc size distributions using image analysis.* Environ. Eng. Sci., 33 (1), 25-34.

SWORSKA, A., LASKOWSKI, J.S., CYMERMAN, G., 2000. *Flocculation of the Syncrude fine tailings Part I and II. Effect of pH, polymer dosage and Mg^{2+} and Ca^{2+} cations.* Int. J. Miner. Process. 60, 143–152.

TARLETON, E.S., WAKEMAN, R.J., 2007. *Pretreatment of suspensions, Solid/Liquid Separation Equipment Selection and Process Design.* 1st Ed, Elsevier Science, Department of Chemical Engineering, Loughborough University, Leics, UK.

TASDEMIR, T., KURAMA, H., 2012. *Fine particle removal from natural stone processing effluent by flocculation.* Environ. Prog. Sustain., 32, 317–324.

TASDEMIR, T., TASDEMIR, A., 2012. *Effect of mixing conditions on flocculation.* Proceedings of XIIIth International Mineral Processing Symposium, Turkey, 831–837.

TASDEMIR, T., TASDEMIR, A., KAKABAYEV, H., 2011. *Evaluation of flocculation process in natural stone processing plant wastewaters by Box-Behnken experimental design.* 22th International Mining Congress, Ankara, 309-315.

TRIPATHY, T., RANJAN, B., 2016. *Flocculation: A new way to treat the waste water.* J. Phys. Sci., 10, 93- 127.

WEBER, W.J., 1972. *Physicochemical Processes for Water Quality Control.* John Wiley and Sons, New York.

WIATR, P., 2019. *The use of filter aids in the gypsum filtration process* - A review of the benefits and the concerns. Nalco.

WICKRAMASINGHE, S., WU, Y., HAN, B., 2002. *Enhanced microfiltration of yeast by flocculation.* Desalination, 147, 25-30.

YARAR, B., 2001. *Evaluation of flocculation and filtration procedures applied to WSRC sludge.* Report no: DE-AC09-96SR18500, Colorado School of Mines, 34.

ZAHRIM, A.Y., AZREEN, I., JIE, S.S., YOIYING, C., FELIJIA, J., HASMILAH, H., GLORIANA, C., 2019. *Nanoparticles Enhanced Coagulation of Biologically Digested Leachate.* Nanotechnology in Water and Wastewater Treatment Theory and Applications Micro and Nano Technologies, 205-241.