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The development of a New Process for Phosphate Thickening

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Abstract

In phosphate beneficiation process, thickening is used to concentrate the slurry or sludge in order to increase its solid content and recover the maximum of water. The addition of flocculants helps to form larger particles that can thicken out quickly. However, the high consumption of flocculant in the thickeners increases the cost of the operation. The purpose of this research is to study the effect of flocculant on sedimentation velocities of different particles size in order to develop a new thickening process which ensure the maximum thickening rate and a minimum flocculant consumption. To achieve this goal, initially the impact of flocculant on different size fraction was studied. The objective of this step is to define the cut-size from which the flocculant has no considerable effect on thickening. This granulometric slice can decant by a simple free sedimentation without needing the flocculant. After that, a hydrocyclone was dimensioned and modeled in order to eliminate this granulometric slice which will undergo free sedimentation. This allowed to design a new thickening technology that targets only fine particles overflow of the hydro-cyclone and that require the addition of flocculant. This technology will significantly reduce the flocculant consumption and ensure a better water recovery in the thickening process.

Keywords: Thickener, Hydrocyclone, Beneficiation, Sedimentation, Solid-liquid separation, Water recovery, Water waste treatment

1. Introduction

Decantation is a process to separate mixtures by removing a liquid layer that is free of a precipitate. Decantation relies on gravity to pull precipitate out of solution. Decantation consists in eliminating sediments, turbidity and suspended solids in untreated sewage by sedimentation. This process is present in many industrial applications such as the sugar industry, mining industry and wastewater treatment [1, 2]. In the phosphate beneficiation processes, the decantation is used to concentrate the washed phosphate or sludge to increase its solids content and also to recycle the recuperated water. The sedimentation is a process in which the force of gravity, hydrodynamics, dispersion, interaction and fractionation forces between particles are considered as competing processes between them. There are different sedimentation pathways that depending strongly on the level of interaction between particles. Thus, if the solid concentration is low, there is little interaction between the particles; therefore the sedimentation mechanism is not influenced. This path is called free sedimentation. However, if the concentration of solid is high, this causes more interaction between the particles and consequently more influence on the sedimentation mechanism. This path is called braked sedimentation. Concerning the free sedimentation, to determine the sedimentation velocity of particles, two different approaches can be followed: an ideal approach in which the particle is considered as sphere. And a second realistic approach in which the particle is considered as natural sediment. In general, the first approach is widely used in literature, especially for the study of sedimentation columns. Although some methods take into account the shape of the sediments. In the literature, many theoretical and empirical equations estimate the velocity of sedimentation. The most used is presented in equation 1.

$$v_p^2 = \frac{4}{3} \times d \times g \times \frac{(\rho_P - \rho_L)}{C_t \times \rho_L} \qquad (1)$$

With :

ρ_P: density of the particle, ρ_L: density of the liquid, C_t: coefficient of drag, v_p: falling speed of the particle, g: acceleration of gravity and d: particle diameter. vp increases as d increases, thus the particle decants faster. The coefficient C_t is a function of the Reynolds number (Re) and the shape of the particle, where :

$$Re = \frac{v_P \times \rho_L \times d}{\mu_L} \qquad (2)$$

It seems impossible to do the calculation of v_p when one needs to know this value to calculate Re and from there to make the choice of the appropriate equation. By algebraic manipulation, we arrive at defining the following criterion:

$$K = d \times \left[\frac{\rho_L \times g \times (\rho_P - \rho_L)}{\mu_L^2}\right]^{\frac{1}{3}} \qquad (3)$$

The table 1 presents the different equations of v_p as a function of coeffcient K and the flow regime.

Table 1. Types of sedimentation velocity equations

K	C_t	Equation	vp
K≤2,6	$\frac{24}{Re}$	Stocks	$v_p = \frac{1}{18} \times g \times \frac{(\rho_P - \rho_L)}{\mu_L} \times d^2$
2,6≤K≤44	$\frac{18,5}{Re^{0.6}}$	Intermediate cases	$v_p = 0.153 \times g^{0,71} \times d^{1,14} \times \frac{(\rho_P - \rho_L)^{0,71}}{\mu_L^{0,43} \times \rho_L^{0,29}}$
45≤K	0.44	Newton	$v_p = 1,74\sqrt{\frac{g \times (\rho_P - \rho_L) \times d}{\rho_L}}$

Concerning the braked sedimentation,as the concentration of suspended particles increases, the particles come closer together and begin to influence each other. The vertical movement of the fluid displaced by the falling of the particles reduces the rate of sedimentation. Generally, the higher the concentration of particles, the more the sedimentation rate

is slowed down with respect to the Stokes velocity of a single particle. There are many ways to deal with this problem. Two of these approaches arrive at an equation of the following form:

$$v = v_S r_l^2 f(r_l) \quad (4)$$

Where v is the braked sedimentation rate, v_S is the Stokes velocity, , r_l is the volume fraction of liquid.

Richardson and Zaki (1954) [3] experimentally studied the sedimentation and fluidization of suspended glass particles in various solutions at different solid concentrations. Their empirical model for the function $f(r_l)$ with low Reynolds number (Re <0.2) is:

$$f(r_l) = r_l^{2,65} \quad (5)$$

The protocols for the distribution of particle fall velocities are based on the gravity column decantation principle. Since the late 1970s, these methods are available [4]. These are simple design instruments that provide estimates of sedimentation velocity of suspended particles. During decantation, the particles settled by gravity at a velocity that depended on their size, shape, weight and concentration [5]. These three methods aim at plotting the falling velocity curve, the curve is a cumulative graph showing the fraction of particles having a falling velocity less than or equal to a given settling speed (Vs). Two categories of methods are generally used for the measurement of the decantation velocity. They are based on column sedimentation but the difference between them is the initial condition of the test [6]: In this literature review, the first method presented is the Victor method. It is a column sedimentation method created in France [7]. The Victor consists of measuring the mass of particles decanted as a function of time. The number of measurements planned for each test is equal to the number of columns used. This method can use up to ten columns at the same time. The advantage of this method is the use of a large sample volume of up to 50 liters to ensure that the sample is representative. But the disadvantage of Victor is to ensure the homogeneity of the starting samples between the different columns. The second protocol is VICPOL and was developed by researchers from the Netherlands [8]. It requires five homogeneous decantation columns for a total sample volume equal to 25 liters. The sample is poured directly into a container with an agitator for homogenize the sample until the test begins. The filling of the columns is done by gravity, the test lasts 24 hours and the sampling is done only once per column (i) each time (ti). The number of measurements to be performed for each test is equal to the number of columns. The disadvantage of this method is the use of sub-samples thus posing the concern of homogeneity of the starting sample, moreover, the method of filling (by gravity) creates thrust forces on the particles at the beginning of the test. The third ViCAs protocol was established in 2009 in France. It was originally designed and validated to estimate the fall velocities of suspended sediments present in runoff [9], with satisfactory results in terms of repeatability and accuracy [10]. However, our interest is its use for the case of wastewater. The ViCAs is a new protocol and has a lot of advantages. It determines the decantation rate of the particles of a sample in a single column unlike the other protocols (VICPOL, VICTOR), the column divides the sample on several subsamples which decreases the homogeneity of the initial sample. The ViCAs requires only 5 liters of sample. Also, the method of filling the sampling (by sprinkling) ensures the distribution of particles over the entire height of the column at the start of the test. The ViCAs protocol is based on the measurement of the mass in suspended matter decanted after different decantation times. It presents a relative uncertainty as to the percentage of the total mass of particles with a falling velocity lower than Vs since tests with a mass balance of ± 15% are accepted. This protocol only requires sieving as pretreatment of the sample before decantation. The ViCAs protocol is based on the principle of homogeneous suspension, under the assumption that the particles decant independently from each other, without forming aggregates and without diffusion [11]. At the time of filling the column of ViCAs: the solids are distributed uniformly over the entire height of the column. With the help of a pump, the sample to be analyzed is sucked into the column. The column is kept under vacuum for the duration of the fractionation. The protocol requires a total water volume of 5 liters, to determine the initial concentration and fill the

settling column which is 65 cm long and 3.5 cm in radius. Sedimentation velocity could be determined by monitoring the optical absorbance at special wavelength as a function of time by ultraviolet-visible spectrophotometer [12]. For particles of a few microns, the sedimentation rate becomes very low. The use of flocculation additives becomes necessary to agglomerate the particles together and thus increase their rate of fall. The flocculants are macromolecular synthetic organic polymers, soluble in water and they are generally in the form of powder. They are differentiated from each other by their molar mass, but especially by the sign and the degree of their iconicity in aqueous solution. The Flocculation have a very important role in the recycling of wastewater, it aims to increase the thickening velocity of the particles of phosphate. The thickening velocity is the index used to evaluate the flocculant effect. In phosphate beneficiation technology, thickening operation is used to concentrate the slurry or sludge in order to increase its solid content and recover the maximum of water. The addition of flocculants helps to form larger particles that can thicken out quickly. The technology used for thickening consumes lots of flocculants. That is why the operation's cost is expensive. This study focuses on the development of a new thickening process. This technology involves the installation of a hydrocyclone before the decanter. This after a detailed study on the impact of flocculant on the different particle size ranges of particles. The hydrocyclone will remove large particles that do not require the addition of flocculant. This technology allows reaching the maximum solid rate with the minimum of flocculants consumption possible.

1. Materials and methods

*1.1. **Phosphate samples preparation***

In the present study we used phosphate particles which constitute the slurry that feeds the industrial thickener, those particles are classified in different sizes : (40 µm, 63 µm, 80 µm, 100 µm, 125 µm, 160 µm, 200 µm, 250 µm, 315 µm, 400 µm, 500 µm) by using a set of AFNOR sieves series to have granulometric classification of the phosphate samples, figure 1, after that the particle size distribution was checked by laser granulometer (figure 2) in order to make sure that the classification was perfect.

Figure 1. Different phosphate particles size samples

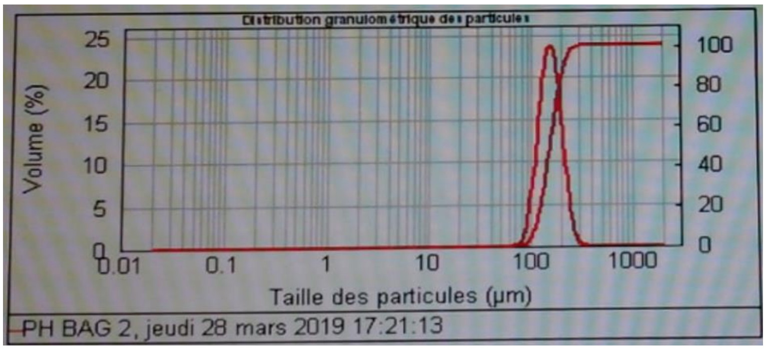

Figure 2. Particles size distribution by granulometry laser

In order to study the effect of flocculant on particles size, several samples were prepared with phosphate particles at different solid concentration. The flocculant used in this study is the polyacrylamide [-CH2-CH(-CONH2)-]n, with a concentration of 5g/L.Final samples and their characteristics are represented below:

Table 2. Characteristic of each sample

Sample	Particles size	Weight (g)	Solid Concentration (w/w)	Flocculant Addition
1	[200 µm,250 µm [	250	22%	Without
2	[160 µm,200 µm [	250	22%	Without
3	[125 µm,160 µm [	250	22%	Without
4	[100 µm,125 µm [	250	22%	Without
5	[80 µm,100 µm [	250	22%	Without
6	[63 µm,80 µm [	250	22%	Without
7	[40 µm,63 µm [	250	22%	Without
8	[200 µm,250 µm [	250	22%	With
9	[160 µm,200 µm [	250	22%	With
10	[125 µm,160 µm [	250	22%	With
11	[100 µm,125 µm [	250	22%	With
12	[80 µm,100 µm [	250	22%	With
13	[63 µm,100 µm [	250	22%	With
14	[40 µm,63 µm [	250	22%	With

*1.2. **Measurement velocity of sedimantation of phosphate particles***

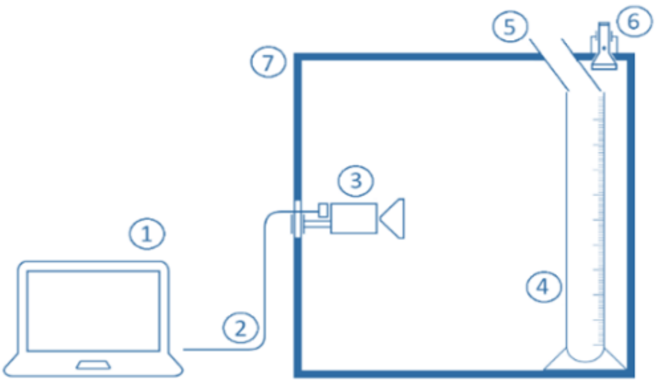

Figure 3. Monitoring device of particles sedimentation

In order to calculate the velocity of sedimentation, we used the device below (figure 3) which includes: (1) laptop, (2) digital camera connection cable, (3) digital camera, (4) graduated test tube of 1L, (5) feeding tube, (6) light source, (7) insulation box. The sedimentation tests were performed in a column with length of 50 cm and, 26mm in diameter and, the velocity of each sample is calculated by the conventional method $v = \frac{\Delta d}{\Delta t}$ using the device shown in figure3 : Where v: the velocity of sedimentation (cm / s), Δd: the distance between the two levels (cm) et Δt: the time required for the sedimentation of all the phosphate particles in (s). We launched the particles in the column

and, measure the time between the instance of launching the sample into water and the instance of stabilization of the solid-liquid interface.

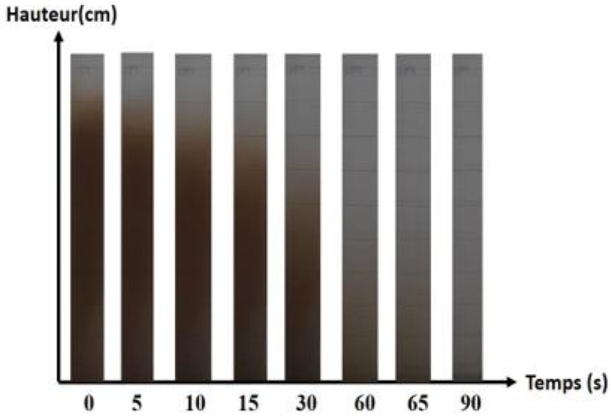

Figure 4. Sedimentation test tube of particles size 63 µm without flocculant

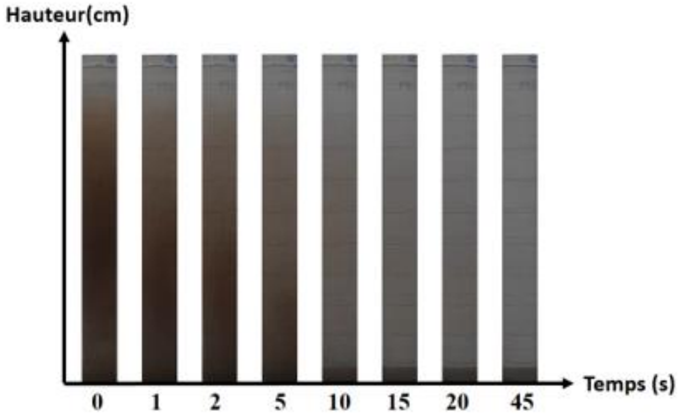

Figure 5. Sedimentation test tube of particles size 63 µm with flocculant

2. Result and discussion

2.1. *Study of flocculant effect on different particles size*

After performing the experiments on different samples, the measurement results of their thickening velocity are shown in the figures bellow :

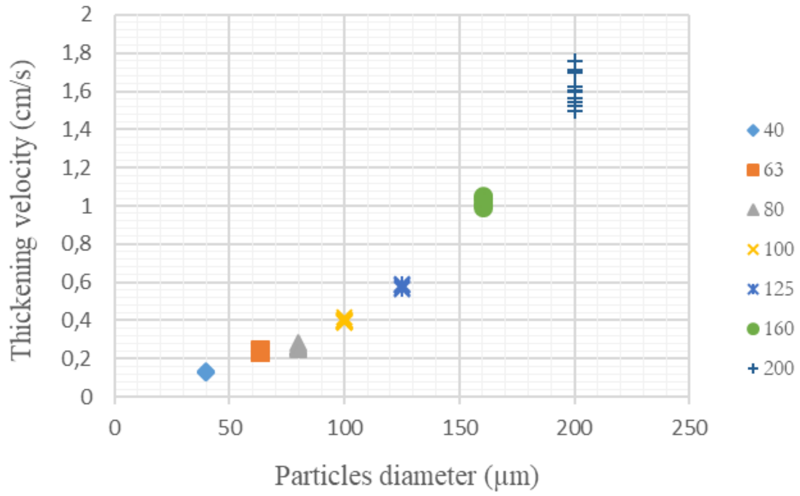

Figure 6. Thickening velocity of samples without flocculant

Without flocculent, the velocity of fine particles is very slow because of their low diameter comparing to the one of coarse particles which is important because of their high diameter. The flocculent has a minimal effect on the sedimentation rate of coarse particles. But for fine particles, the flocculent influences the rate of sedimentation considerably. In order to well visualize and compare thickening velocities with and without flocculant the measurement results of thickening velocities are gathered in one figure

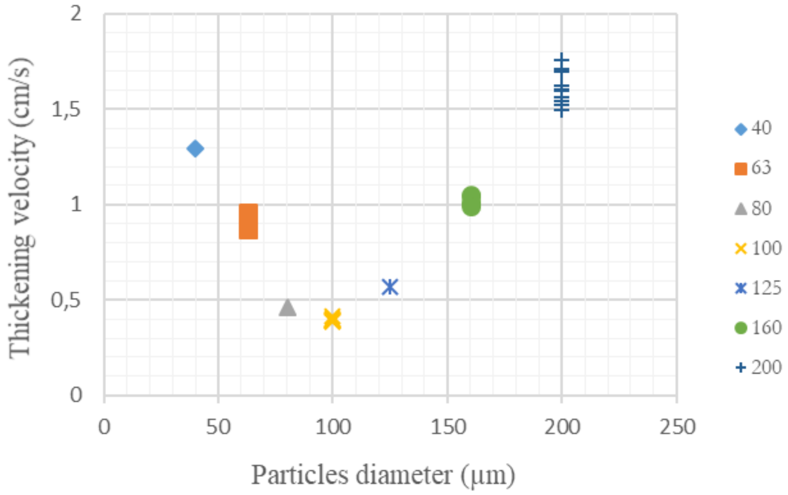

Figure 7. Thickening velocity of samples with flocculant

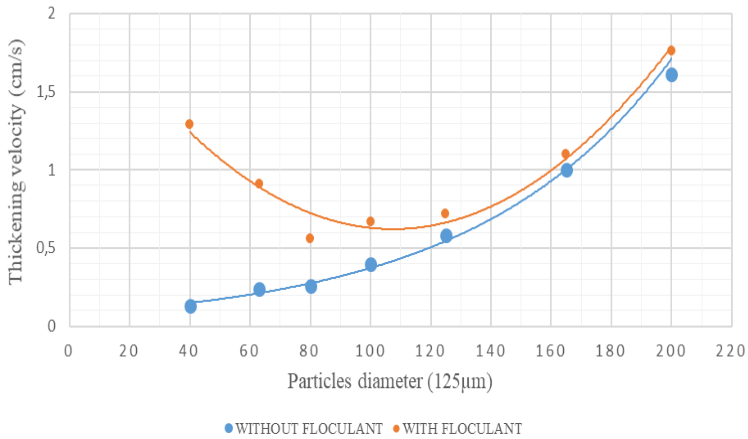

Figure 8. Thickening velocity of different samples

The study of particles sedimentation velocity of different particles size with and without flocculant shows that the flocculant has an important effect on particles less than 125 µm in our case, which prouves the imperative using of flocculant to improve the thickening process on fine particles. However, the effect of flocculant on particles having a diameter bigger than the cut-size mentioned before remains almost the same. In order to optimize the flocculant consumption in slurry with different particles sizes, it is necessary to separate them. To take advantage of this result, we proposed to separate particles using a hydro-cyclone that will ensure a separation at specific particle size. The Prediction of the hydro-cyclone underflow and overflow will be performed using a calibrated Plitt model, representing a real hydro-cyclone realizing a cut-size of 125µm.

*2.2. **Hydrocyclone modeling and simulation***

The higher usage of hydro-cyclones in the 1950s and 1960s has led to a development of correlations facilitating their dimensioning and the simulation of their behavior. Empirical models based on experimental data regression are the more used in order to size hydro-cyclones and predict their performances. The first experiments w realized in the 1960s by Lynch [13,14], using hydrocyclone with a diameter of (500mm, 3800mm,100mm) and particles of silica, copper and limestone at a solid concentration between 15wt% 70wt%. The most used empirical model is the one developed in 1975 by Plitt [15], using the experimental data collected by Lynch and Rao (1975) and other concerning cyclones with a smaller diameter (31mm, 63mm and 152mm) operating up to a solid concentration of 13%. This model is based on four empirical equations that relates the corrected particle size Dc50, Plitt factor m, feed pressure P, the ratio S of the underflow volumetric flowrate to the overflow flowrate of slurry S, to the operating conditions and hydro-cyclone sizes as following :

$$P = a_1 \frac{Q^{1.46}.\exp(-7.63\phi + 10.79\phi^{1.46})}{DC^{0.2}.h^{0.15}.DI^{0.51}.DO^{1.65}.DU^{0.58}} \quad (6)$$

$$d_{50c} = a_2 \frac{DC^{0.44}.DI^{0.58}.DO^{1.91}.\exp(11.12\phi)}{DU^{0.8}.h^{0.37}.Q^{0.44}.(\rho s-1)^{0.5}} \quad (7)$$

$$S = \frac{Q(U)}{Q(O)} = a_3 \frac{h^{0.19}.(\frac{DU}{DO})^{2.64}.\exp(-4.33\phi + 8.77\phi^2)}{P^{0.54}.DC^{0.37}.Q^{0.44}.(\rho s-1)^{0.5}} \quad (8)$$

$$E_{ic} = 1- \exp(-0.693(\frac{d_i}{D_{50c}})^m) \quad (9)$$

$$m = \exp(a_4 - 1.58 * \frac{S}{S+1})(\frac{DC^2.h}{Q})^{0.15} \quad (10)$$

$$B_{pf} = \lambda B_{pw} \quad (11)$$

$$B_{pw} = \frac{\frac{S}{S+1} + \phi R_{sc}}{1-\phi[1-\lambda(1-R_{sc})]} \quad (12)$$

$$R_{sc} = \sum_{k=0}^{n} f_i E_{ic} \quad (13)$$

The following data (table 2, 3 and4) relative to a hydrocyclone operating with a with a cut size of 125µm has been used in order to calibrate the Plitt model :

Table 3. Operating conditions and hdyrocyclone size

	Inlet	Underflow	Overflow
Flowrate (m3/h)	535.6	47.5	488.2
Solid concentration (w%)	12.9	29.6	11.2
Solid density (ton/m3)	2.9		
Feed pressure (bar)	2		
Number of hydro-cyclones	3		
DC (mm) cyclone diameter (in)	500		
h (mm) cyclone height (in)	1935		
DI (mm) cyclone inlet diameter (in)	150		
DO (mm) cyclone vortex diameter (in)	167		
DU (mm) cyclone apex diameter (in)	40		

The hydrocyclone described above performs a phosphate particles separation exactly under the desired cut size. Samples from the hydrocyclone feed, underflow and overflow were extracted and analyzed using a granulo-laser. Results of the analyses of different particles size distribution are represented in table 4.

Table 4. Particles size distribution of the hydrocyclone inlet

Opening (µm)	Passing (%)		
	Inlet	Underflow	Overflow
0	--	--	--
40	38.2	13.6	44.5
50	40.7	14.7	47.4
63	49	19.1	56.7
80	58.6	26.3	66.9
100	80.8	52.5	88.1
125	92.3	74.9	96.8
160	99.5	97.6	99.9
200	100	100	100

The calibration parameters are obtained by resolving Plitt model equations, using the hydrocyclone sizes and using the properties of the inlet and the outlet of the cyclone. These calibration parameters are represented table 5: In order to the study the particles size effect on sedimentation efficiency, a hydrocyclone is sized to achieve a separation of particles at cut-size of 125 µm. The simulation of the hydrocyclone is performed using the calibrated model. The parameters of the thickener feed are: Flow rate of 2500 m^3/h; solid density of 2.9 ton/m^3; and solid concentration of 22w%. As shown in the figure 9, the calculated cut-size is about 126,2 µm which corresponds to the cut-size of 125 µm previously fixed.

Table 5. Plitt model callibration parameters

a1	a2	a3	a4	λ	P (bar)
7,908	7,517	51,110	0,596	1,049	2

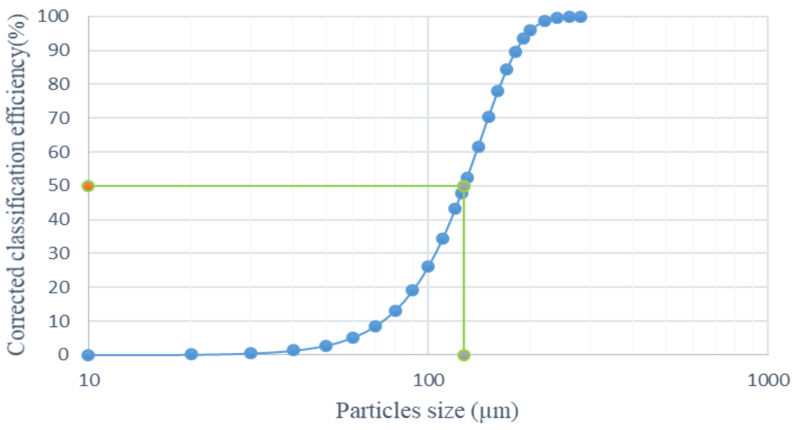

Figure 9. Hydrocyclone separation efficiency curve

The simulation results of the thickener feed classification using Plitt model is summered in the table 6.

Table 6. PSD of hydrocyclone inlet, underflow and overflow

Opening (µm)	**Passing (%)**		
	Inlet	**Underflow**	**Overflow**
600	100	100	100
500	99.96	99.92	100
400	99.57	99.13	100
315	97.38	94.61	100
250	92.25	84.07	100
210	86.24	71.76	99.96
200	84.28	67.83	99.88
160	73.17	46.91	98.06
150	69.81	41.48	96.69
125	59.76	27.97	89.91
100	48.67	17.76	77.98
80	39.54	12.25	65.42
74	36.42	10.77	60.76
63	32.52	9.18	54.66
53	28.62	7.83	48.34
44	26.07	7.04	44.12
40	24.84	6.67	42.06
37	24.32	6.53	41.20
0	--	--	--
Solid concentration (w%)	22	52.6	142

*2.3. **Study of particles separation effect on thickening efficiency***

In order to study the effect of particles separation on thickening efficiency, Plitt model was calibrated and used to simulate slurry classification to predict the underflow and overflow composition. Sedimentation tests were performed using different prepared phosphate samples based on hydro-cyclone results (PSD and solid concentration). The same flocculant polyacrylamide [-CH2-CH(-CONH2)-]n, with a concentration of 5g/L, was used during the tests. The sample's characteristics are shown below :

The figure 10 shows the sedimentation velocity of the sample 1 (feed with Flocculant) and the sample 5 (OF with Flocculant + UF without Flocculant). The Sedimentation velocity of the raw feed (without cyclone) is about 2 cm/s. In the experiment 5, the addition of the flocculant only to the hydrocyclone overflow improves significantly the sedimentation velocity (about 3 cm/s). In this case the amount of flocculant consumed is significantly reduced. This justifies also the results obtained in Figure 5.

Table 7. Samples characteristic

Sample	Description	Solid Weight (g)	Solid (w/w%)	Concentration	Flocculant Addition
1	Inlet	22	22		With
2	Underflow	10.5	52.6		With
3	Overflow	11.5	14.2		With
4	Underflow	10.5	14.2		Without
5	(3)+(4)	22	52.6		OF with Flocculant+ UF without Flocculant

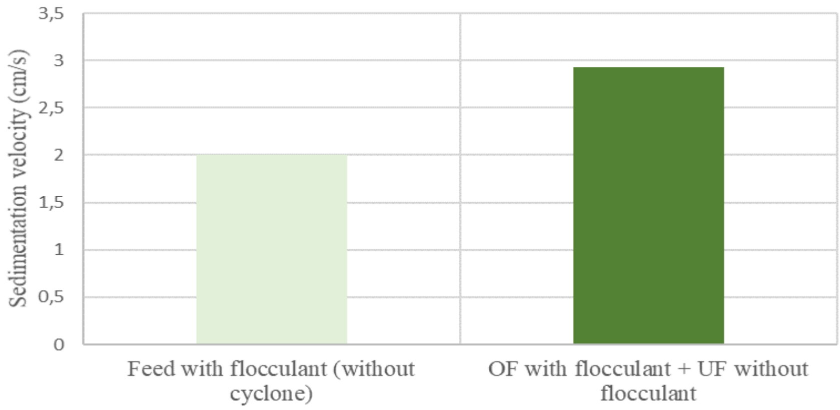

Figure 10. Sedimentation velocity comparison and process validation

3. Conclusion

The study of particles sedimentation velocity of different particles size with and without flocculant shows that the flocculant has an important effect on particles less than a specific size of 125µm. Beyond this specific size the flocculant has no considerable effect on thickening. The particles larger than 125µm can decant by a simple free sedimentation without needing the flocculant. To achieve that, a hydrocyclone was dimensioned and modeled in order to eliminate this granulometric ranges which will undergo free sedimentation. This new developed hybrid technology (Thickener coupled Hydrocyclone) allows to target only fine particles overflow of the hydro-cyclone that require the addition of flocculant. In this study, the new developed process can reduce the consumption of flocculant by 50%.

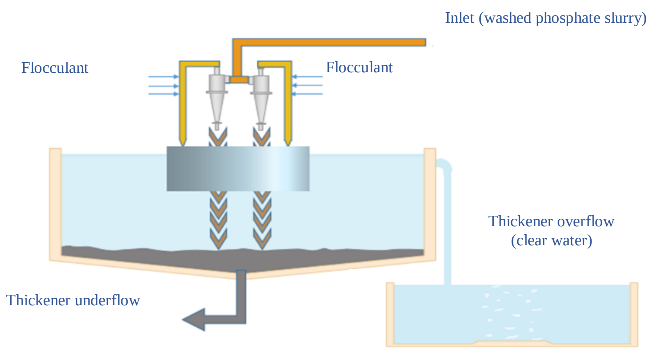

Figure 11. The proposed thickening process

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