

Analytical method for determining the saturation point of superplasticizers in cement pastes using the Marsh cone

(Método analítico de determinação do ponto de saturação de superplastificantes em materiais cimentícios usando o cone de Marsh)

O. F. da Silva^{1*}, P. C. C. Gomes^{1,2}, K. A. M. Morais²

¹Federal University of Alagoas, PPG-Materiais, Maceió, AL, Brazil

²Federal University of Alagoas, CTEC/LEMA, Maceió, AL, Brazil

Abstract

The optimum dosage of superplasticizer (SP) additives is determined by the saturation point of SP (SPS), obtained on cement paste by the utilization of the Marsh cone. Obtaining the SPS is important because it defines the amount of SP that should be used in concrete dosages when it is necessary the reduction of water demand and the improvement of the workability. The SPS is determined by methods that use the angles defined by the slope of the flow curve, which are obtained through geometric and visual resources. However, depending on the curve shape, these methods can provide inaccurate results. For this reason, this study analyzed the utilization of the existent geometric methods and proposed a new analytic method of SPS determination. It is noteworthy that the proposed analytical method (PAM) was developed by a numerical implementation to obtain the representative function of paste flow. The SPS is determined from the solution of the phenomenon differential equation and can be used linked to a computational environment in concrete composition calculation. PAM was applied and evaluated in different flow curves obtained by several authors.

Keywords: superplasticizer, saturation point, Marsh cone, analytical method.

Resumo

A dosagem ótima dos aditivos superplastificantes (SP) é determinada pelo ponto de saturação do SP (PSP), obtido na pasta de cimento pela utilização do cone de Marsh. A obtenção do PSP é importante, pois define a quantidade de SP que deve ser utilizada em dosagens de concretos, quando são necessárias a redução da demanda de água e a melhoria da trabalhabilidade. O PSP é determinado por métodos que usam os ângulos definidos pela inclinação da curva de fluxo, que são obtidos através de recursos geométricos e visuais. No entanto, dependendo da forma da curva, esses métodos podem fornecer resultados imprecisos. Por este motivo, este estudo analisou a utilização dos métodos geométricos existentes e propôs um novo método analítico de determinação do PSP. Ressalta-se que o método analítico proposto (MAP) foi desenvolvido por implementação numérica para obter a função representativa do fluxo das pastas. O SPS é determinado a partir da solução da equação diferencial do fenômeno, e pode ser utilizado ligado ao ambiente computacional no cálculo da composição do concreto. O MAP foi aplicado e avaliado em diferentes curvas de fluxo obtidas por diversos autores.

Palavra-chave: superplastificante, ponto de saturação, cone de Marsh, método analítico.

INTRODUCTION

The use of superplasticizer (SP) additives is common in the concrete production, especially when the following are required: an increase of workability and resistance to compression, and a reduction of the water/cement (w/c) ratio [1-3]. It is verified that to obtain special concretes, such as high-performance concrete (HPC) and self-compacting

concrete (SCC), the utilization of SP is indispensable [1, 4, 5]. In the literature, it is observed that the SP utilization and research are not new and has been studied since the '80s [2, 3, 5, 6]. Aïtcin [6] asserts that when in contact with water, the cement particles have a strong tendency to flocculation. Consequently, part of the water is trapped among the grains of cement, reducing the water availability and the particle lubrication. Therefore, the mixture viscosity is increased, reducing the specific area of cement grains and diminishing the water available for hydration reactions [7].

The SP dosage depends on several factors: type of

*osvaldoferr@gmail.com

<https://orcid.org/0000-0001-7126-5311>

cement, shape and dimension of fines, w/c ratio, type of SP, compatibility between cement and SP, as well as the temperature and humidity of the materials and the environment [4-8]. In the SP literature, it can be seen that there is an optimum dosage of SP for each kind of composition, and for many times, there are differences from those ones proposed by the manufacturer [9, 10]. It is verified, that the determination of optimum dosage of SP is usually carried out in tests with cement pastes, considering that the main action is on the particles of cement and additions. This determination influences directly the fluidity and fresh concrete properties [4, 6]. Moreover, from these tests, information about the cement incompatibility, mineral additions, and other chemical additives, quality and efficiency of SP can be collected [9-12]. The test methods used for obtaining the SP dosages are those that are based on rheological properties by the rheometer [13, 14], from the flow curves using the Marsh cone [3, 4, 6, 7, 11, 12], and from spreading tests by mini-slump [4, 5, 15]. Due to the simplicity of apparatus and procedures, Marsh cone test of the pastes and mortar has become a widely used method. It is used to determine the flow curve for different points that represents the sample fluidity time versus the SP content, determined in percentage terms [16]. The Marsh cone used in tests has a relation of 2:1, between the height and the top opening diameter (Fig. 1).

Saturation point of superplasticizer (SPS): the SP dosages are calculated by the relationship between the amount of cement and the solid content of the superplasticizer, defined in percentage terms (% SP/c) [1, 4, 6]. The SPS is defined as the percentage of superplasticizer from which, even adding more SP, the improvement in paste flow characteristics is insignificant and may even be impaired [3-5, 8, 17]. The graphs representing the flow test of the pastes and mortar using the Marsh cone generally have well-defined behavior and approximate to a decreasing exponential curve, where the x-axis is the percentage of SP and the y-axis is the flow time (Fig. 2). The SPS is located at the point near the horizontal asymptote of the flow curve [8, 7, 10]. It is

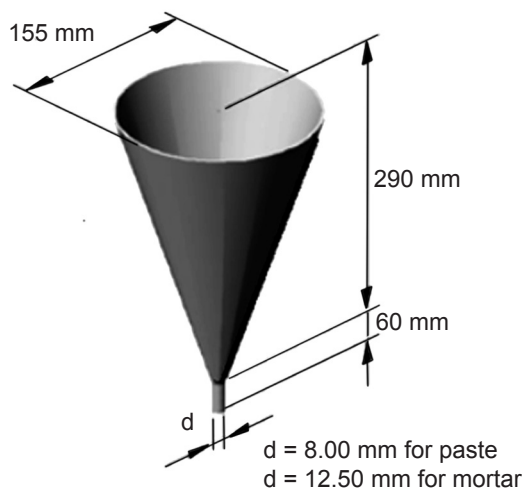


Figure 1: Details of Marsh cone.

[Figura 1: Detalhes do cone de Marsh.]

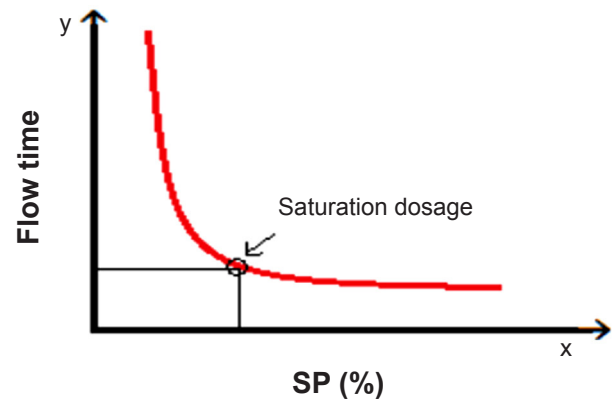


Figure 2: Location point of saturation of the superplasticizer (SPS). [Figura 2: Localização do ponto de saturação do superplastificante (PSP).]

verified that the SPS is a reference point that can be found in the interval of the change of direction of the flow curve, and it can be considered as any point within this region.

The concrete dosage is defined by fix amount of materials, and for this reason, the determination of a single reference point for the SPS is important. Therefore, to determine the SPS location in the curve, it is necessary an accurate methodology. For this reason, some methods were proposed and can be found in the literature: Aïtcin [6], AFREN De Larrard [7], Gomes [10], and that suggested by ASTM C939/2010 [18] (Fig. 3). The method of Aïtcin [6] consists of the repetition of the Marsh cone test in times of 5 to 30 min. The intersection point of the lines that represent the tests in these times determines the SPS (Fig. 3a). This method is characterized for analyzing the paste fluidity loss, which is important when a longer time of applications is required, mainly, on the compatibility analyses among the paste's constituent materials. It was observed that this method does not consider any mathematical model that defines the SPS objectively. The AFREM De Larrard method (1997) deals the phenomena of the cement material flow using the Marsh cone; the results are analyzed by a graphic that shows the SP/c ratio (%) - x, versus the flow time logarithm, $\log T$ - y (Eq. A). The SPS is defined as the abscissa point that is tangent of a right triangle of sides 2 and 5, for the flow curve (Fig. 3b).

$$\log T = f(\%SP/c) \quad (A)$$

The ASTM C939 method [18], similarly to the AFREM De Larrard method [7], recommends that SPS be the tangent point to the hypotenuse of a triangle rectangle with angles of 30° and 60° (Fig. 3c). It can be observed that the use of the method proposed by ASTM C939 [18] provides values lower than those proposed by De Larrard [7] for SPS. This is because the method proposed by ASTM [18] defines a higher angle of inclination with respect to the horizontal. The method of Gomes [10] defines to plot the flow curve in the graph for the $\log T$ - y, as a function of the SP/c (%) - x, and

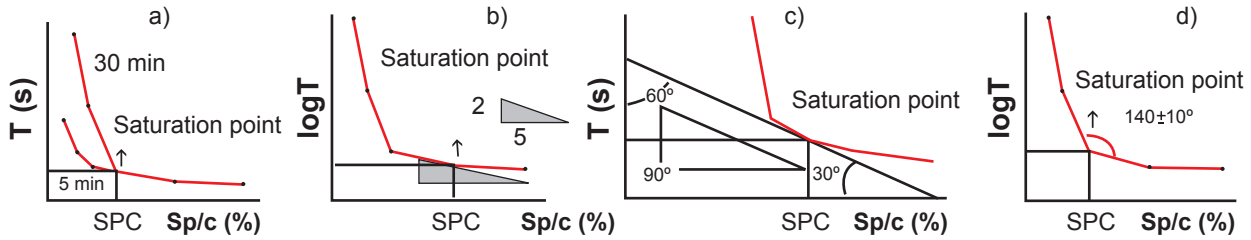


Figure 3: Determination of SPS by: a) Aitcin [6]; b) AFREN [7]; c) ASTM C939/2002 [18]; and d) Gomes [10].
 [Figura 3: Determinação do PSP por: a) Aitcin [6]; b) AFREN [7]; c) ASTM C939/2002 [18]; e d) Gomes [10].]

from the union of the points by line segments the SPS should be the first point that forms an angle $\alpha=140^\circ\pm 10^\circ$ (Fig. 3d). In this method, the lines converge to the point considered (SPS) creating an angle, which the tangent must be $-0.577 \geq \text{tg}\alpha \geq -1.192$. The angles that can be identified as SPS are shown in Fig. 4. The α angles obtained from the results of flow curves can be calculated by Eq. B. Moreover, in this equation, the θ angles are determined by Eq. C.

$$\alpha_n = (\theta_{n+1} - \theta_n) + 180^\circ \quad (B)$$

$$\theta_n = \text{arctg} \left(\frac{y_n - y_{n+1}}{x_{n+1} - x_n} \right) \quad (C)$$

The SPS determination through the shown methods, in general, uses geometric and visual resources to define this reference point. In some cases, these geometric methods are not accurate and can identify more than one SPS inside the transition region of the flow curve; generally, the smallest value of dosage is chosen. It is noteworthy the flow curve shape may not be suitable to apply these geometric methods and is necessary to find another way to measure the SPS. Moreover, another disadvantage of applying these methods is related to the difficulty of implementation on the computational environment. In this sense, this study proposes an analytical method for determining a single

point of reference for the SPS, from the flow curve of cementitious materials obtained by the Marsh cone. This method uses the differential equation of the phenomenon and has the ease of computational implementation as an advantage.

PROPOSED ANALYTICAL METHOD

The proposed analytical method (PAM) was developed from the study of the flow curves, obtained from results of pastes using Marsh cone tests. This analysis allowed obtaining an analytical method for the determination of the SPS using basics concepts of infinitesimal calculus, and computational implementation by the utilization of software's based on the least squares method (LSM). This resource is widely used to solve engineering problems [19] and it was used in this work, allied with the commercial software's Origin Pro 8 and MAPLE. From the analysis of SP/c (%) versus logT for the flow curves of pastes using the Marsh cone, it was observed that the curves behavior can be described by a descendant exponential function, given by Eq. D. It is verified that the coefficients A_1 and y_0 are units of time, and t_1 is the percentage of SP solids divided by the cement mass (%SP/c). In this equation, A_1 , t_1 and y_0 are constants parameters for each test curve. Moreover, from the function of the phenomenon (Eq. D), it is possible to calculate its derivative given by Eq. E. The SPS is determined by solving the Eq. F, the derivate value equal to $\text{tg}150^\circ = -\text{tg}30^\circ = -0.57$, slope defined by the ASTM C939 [18] as shown in Fig. 5. Moreover, this reference point to obtain the SPS is identified by a unique form and it gives values that are within the values proposed by Gomes [10] and the ASTM C939 [18]. It is observed that the values provided by PAM are lower than those obtained for the AFREM De Larrard (1997) method, for the same material. It is verified that the PAM provides the possibility to identify points with angles of tangency lower than those proposed by the geometric methods. In this case, a reference point is the lower limit proposed by Gomes [10], $\text{tg}\alpha = \text{tg}140^\circ = -0.83$, which can be chosen. If used, it creates the possibility of obtaining lower values for the SPS. On the other hand, it is observed that using the value proposed by AFREM De Larrard [7], $\text{tg}\alpha = -0.40$, the obtained SPS is higher.

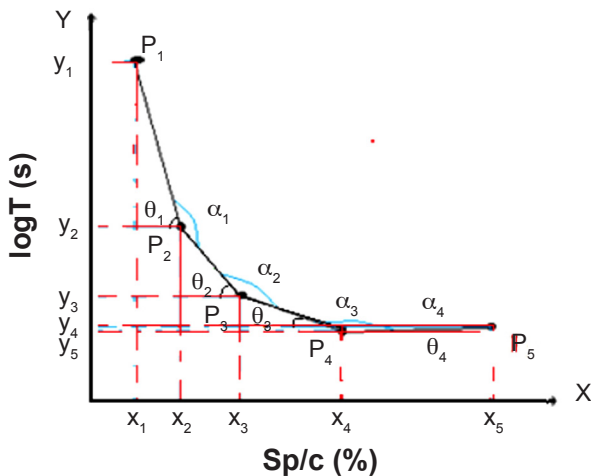


Figure 4: Determination of SPS using the method of Gomes [10]; adapted from [10].
 [Figura 4: Determinação do PSP usando o método de Gomes [10]; adaptado de [10].]

$$f(x) = A_1 \cdot e^{-\left(\frac{x}{t_1}\right)} + y_0 \quad (D)$$

$$\frac{dy}{dx} = -A_1 \cdot \left(\frac{e^{-x}}{t_1} \right) \quad (E)$$

$$\frac{dy}{dx} = -A_1 \cdot \left(\frac{e^{-x}}{t_1} \right) = -0.57 \quad (F)$$

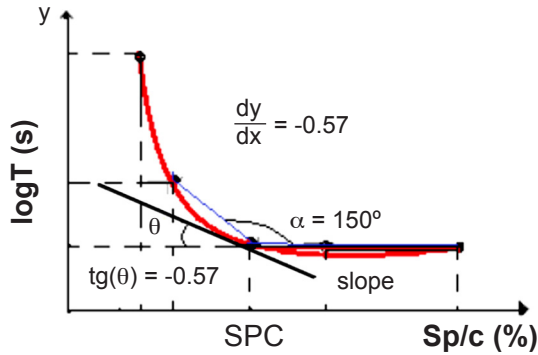


Figure 5: SPS of PAM according to the adjustment of the decreasing exponential curve.
 [Figura 5: PSP do MAP de acordo com o ajuste da curva exponencial decrescente.]

MATERIALS AND METHODS

The materials with their characteristics and compositions, used in the preparation of the pastes used for PAM verification, are presented in Table I. The pastes produced with the presented materials are important for obtaining special concretes like the self-compacting concrete (SCC). In the SCC it is common to use filler to improve its viscosity. In this study, the residue of marble and granite processing (RMGP) was used with a maximum particle diameter of 0.15 mm as a filler.

Method of sample preparation: the pastes were produced

in a 5 L capacity mortar mixer, producing a constant volume of 1.20 L of paste, with the following procedure: the mixer and blade were wetted, then the cement and the mineral additions were mixed at slow speed for 30 s. It was placed 80% of the water and mixed at slow speed for 60 s. The mixer was cleaned for 30 s, afterward the SP and the rest of the water was mixed at slow speed for 30 s, then at rapid speed for 150 s.

Test method: the tests were carried out with the same paste volume of 1.00 L; the time of flowing through the Marsh cone of a constant volume of 500 mL was determined. The tests were performed with the temperature between 27 and 29 °C and relative humidity between 65% and 70%.

RESULTS AND DISCUSSION

Besides test data, other results from the literature were used in the PAM application. Table II presents the results obtained from one of the tests, for an initial and detailed demonstration of PAM. Using the data of Table II, it was possible to represent the phenomenon of flow curve, shown in Fig. 6. From the showed methods to obtain the SPS (Fig. 3), it was observed that the value found by AFREM De Larrard [7] was between the SP dosages of 0.40% and 0.50%. On the other hand, from the Eqs. B and C using the Gomes method [10], it was possible to obtain the α angles of the flow curve and the θ inclinations of the lines with the corresponding horizontal axis (Table III). It was observed from the results of Table III that the angle which determined the SPS within the gap of $140^\circ \pm 10^\circ$ cannot be found. However, it was reasonable to accept that SPS can be considered in the range of 0.45% to 0.50%. According to the ASTM C939 [18], the SPS can be determined within the gap between 0.45% and 0.50%. Thus, it is verified that the existing geometric methods converge to a SPS value in the gap between 0.40% and 0.50%.

Applying the PAM using the data from Table II, the curve of Fig. 7 was obtained together with the function

Table I - Characteristics of materials and parameters considered.
 [Tabela I - Características dos materiais e parâmetros considerados.]

Ratio w/c	RMGP (%)	Cement (CPII-F-32) ρ (g/cm ³)	RMGP ρ (g/cm ³)	Water ρ (g/cm ³)
0.50	0.50	3.15	2.65	1.00
Characteristics of SP				
Color	ρ (g/cm ³)	Solid fraction (%)	Chemical base	Viscosity η (cps)
Cloudy white	1.08	30.00	Carboxylate ether	<125
Quantity of materials used to obtain 1.5 L of paste				
SP/c (%)	SP (g)	Cement (kg)	RMGP (kg)	Water (kg)
0.20	10.14	1.52	0.76	0.75
0.40	20.29	1.52	0.76	0.74
0.60	30.43	1.52	0.76	0.73
0.80	40.58	1.52	0.76	0.72

Table II - Results of the tests in the Marsh cone applied to determine the flow curve.

[Tabela II - Resultados dos testes no cone Marsh aplicados para determinar a curva de fluxo.]

SP/c (%)	Time (s)	LogT
0.20	118.00	2.07
0.40	16.00	1.20
0.60	14.00	1.15
0.80	13.95	1.14

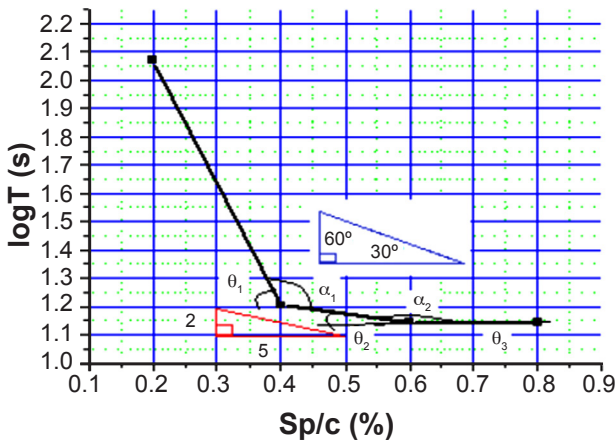


Figure 6: Flow curve to the SP using the results of Table II. [Figura 6: Curva de fluxo para o SP usando os resultados da Tabela II.]

Table III - Results of the Gomes method [10] application. [Tabela III - Resultados da aplicação do método de Gomes [10].]

SP/c (%)	LogT	tgθ	θ (degree)	α (degree)
0.20	2.071	-	-	-
0.40	1.204	-4.335	77.05	119.13
0.60	1.146	-0.290	16.18	164.68

parameters suggested to the problem modeling. According to the parameters A_1 , t_1 and y_0 calculated by LSM and from the application of the function proposed by PAM, the Eq. G was obtained. PAM identifies the SPS as the percentage of SP/c ratio, and the point which the derivative function of flowing phenomenon for the cementitious material dy/dx is equal to -0.57 (Eq. H). It was observed that the SPS is a solution of Eq. H. Therefore, the x value calculated by SPS was equal to 0.43% . This value of SPS was near to the values obtained by the geometric methods, showing that PAM was successfully used. Analyzing the Eq. G, from dimensional and physical aspects, for the values of $x=0$ and $y=1.38 \times 10^{15}$ s, it was verified that this paste does not flow through the Marsh cone considering a percentage of SP equal to 0. On the other hand, considering a high amount of SP, it was observed that there is a trend of flowing time so that the

paste reaches a minimum limit. For this case, according to Eq. I, $T=13.86$ s, provided that segregation of paste does not occur, this may cause a slight increase in flow time. It was observed that this value was very close to the experimental flow time of $T=13.95$ s.

$$y = 13.999 \cdot e^{\left(\frac{-x}{0.073}\right)} + 1.142 \quad (G)$$

$$\frac{dy}{dx} = -189.883 \cdot e^{-13.565 \cdot x} = -0.57 \rightarrow x = 0.43\% \quad (H)$$

$$\lim_{x \rightarrow \infty} (y) = 1.142 \rightarrow \log y = 1.142 \rightarrow y = 13.86 \text{ s} \quad (I)$$

The verification of the applicability and efficiency of PAM was carried out from the analysis of several cement materials (pastes and mortars) manufactured in the laboratory (LEMA/UFAL), as well as data obtained from the analysis of studies of the existing literature, as presented in Tables IV to VII. From Fig. 8, it is observed that the flow behavior of cementitious material by using the Marsh cone was well defined. The curves created by downward straight lines had the slope dependent on SP dosages, which in turn depended on the w/c ratio and the additions. It is noteworthy that the curves obtained from the fit of test points showed an elongated shape behavior, with bigger curvature radius, or upright with a smaller curvature. The most elongated shape of the curve makes it difficult to identify the SPS by geometric methods, and it may not be possible to determine it, as seen in the curve behavior of paste test data 3 and 4. Thus, it was verified that more than one point could be identified for the SPS, which may generate an inaccurate result for this reference point.

For the PAM application in the test data of the cementitious materials indicated in Tables IV to VII, the parameters A_1 , t_1 and y_0 were initially calculated. These function parameters are shown in Table VIII. It was observed that the function defined for modeling the problem showed a correlation coefficient (r^2) higher than 0.979, showing great

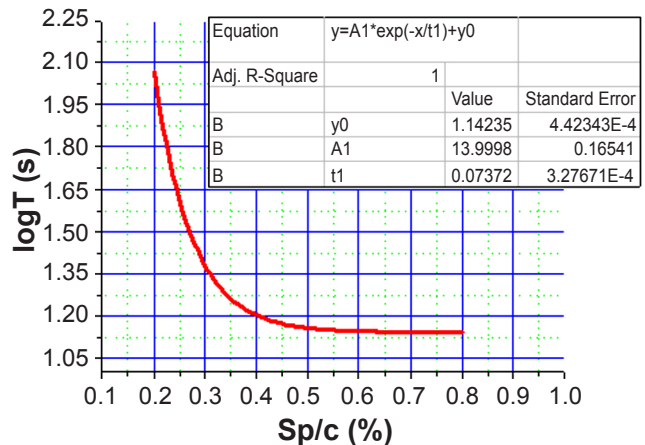


Figure 7: Function and representative curve of the phenomenon. [Figura 7: Função e curva representativa do fenômeno.]

Table IV - Results of Marsh cone tests of the pastes 1 to 4 (LEMA/UFAL).

[Tabela IV - Resultados dos ensaios de cone de Marsh das pastas 1 a 4 (LEMA/UFAL).]

Paste 1		Paste 2		Paste 3		Paste 4	
SP/c (%)	LogT	SP/c (%)	LogT	SP/c (%)	LogT	SP/c (%)	LogT
0.15	1.331	0.25	1.279	0.15	1.335	0.05	0.955
0.25	1.225	0.60	1.068	0.25	1.265	0.10	0.903
0.30	1.221	0.80	1.061	0.30	1.235	0.15	0.878
0.35	1.220	1.00	1.064	0.35	1.215	0.20	0.863
0.45	1.215	-	-	0.40	1.205	0.25	0.858

Table V - Results of Marsh cone tests of the pastes 5 to 8 [12].

[Tabela V - Resultados dos ensaios de cone de Marsh das pastas 5 a 8 [12].]

Paste 5		Paste 6		Paste 7		Paste 8	
SP/c (%)	LogT	SP/c (%)	LogT	SP/c (%)	LogT	SP/c (%)	LogT
0.075	1.25	0.08	1.43	0.075	1.73	0.10	1.59
0.12	1.18	0.10	1.32	0.10	1.53	0.13	1.34
0.20	1.13	0.25	1.15	0.25	1.15	0.15	1.25
0.50	1.11	0.50	1.05	0.45	1.06	0.20	1.08
1.00	1.11	1.00	1.03	1.00	1.05	0.50	1.03

Table VI - Results of Marsh cone tests of the mortars 9 to 12 [7].

[Tabela VI - Resultados dos ensaios de cone de Marsh de argamassas 9 a 12 [7].]

Paste 9		Paste 10		Paste 11		Paste 12	
SP/c (%)	LogT	SP/c (%)	LogT	SP/c (%)	LogT	SP/c (%)	LogT
0.18	1.58	0.08	1.73	0.20	1.45	0.30	1.75
0.20	1.43	0.10	1.54	0.22	1.33	0.35	1.35
0.23	1.30	0.12	1.16	0.25	1.20	0.45	1.23
0.25	1.13	0.20	1.10	0.30	1.15	0.50	1.20
0.34	1.03	0.25	1.08	0.36	1.10	0.60	1.15
0.50	1.03	1.00	1.07	1.00	1.09	1.00	1.14

Table VII - Results of Marsh cone tests of the pastes 13 to 16 [10].

[Tabela VII - Resultados dos ensaios de cone de Marsh das pastas 13 a 16 [10].]

Paste 13		Paste 14		Paste 15		Paste 16	
SP/c (%)	LogT	SP/c (%)	LogT	SP/c (%)	LogT	SP/c (%)	LogT
0.90	2.36	0.60	2.12	0.30	1.78	0.20	2.04
1.00	2.29	0.70	2.03	0.40	1.64	0.30	1.50
1.20	2.26	0.80	2.02	0.50	1.63	0.50	1.42
1.50	2.24	1.00	2.01	0.80	1.61	0.80	1.40
2.00	2.24	-	-	-	-	-	-

compatibility with the studied phenomenon. The curves obtained with the functions with parameters presented in Table VIII are presented in Fig. 9.

From this study, it was verified that regardless of the curve shapes it was always possible to determine a single reference

point for the SPS using PAM (Table IX). The values obtained with the use of the PAM, in general, were close to those found by the methods of Gomes [10] and ASTM C939 [18]. Depending on the shape of the curve it was not possible to identify the angle predicted by the Gomes method [10], and

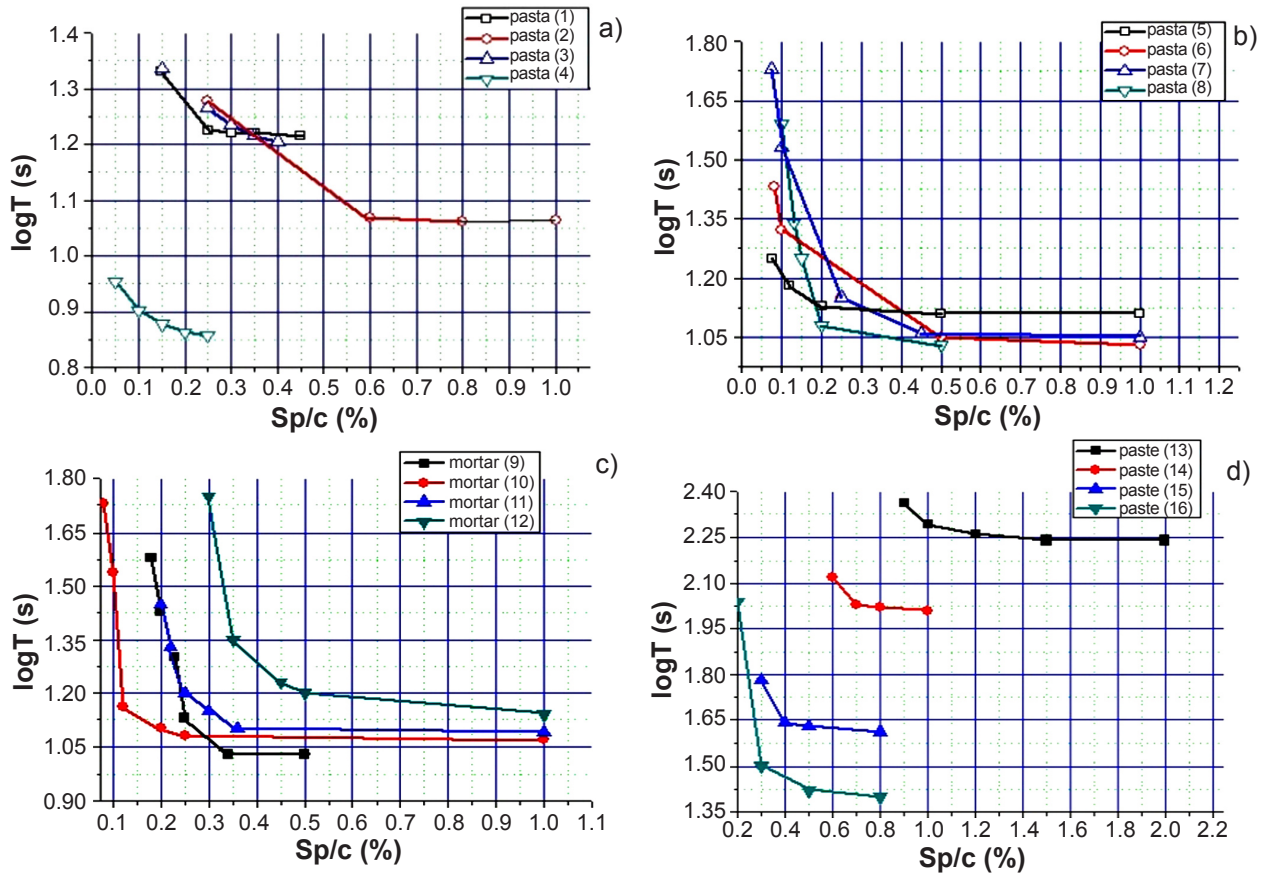


Figure 8: Flow curves of tests 1 to 16.
 [Figure 8: Curvas de fluxo dos ensaios 1 a 16.]

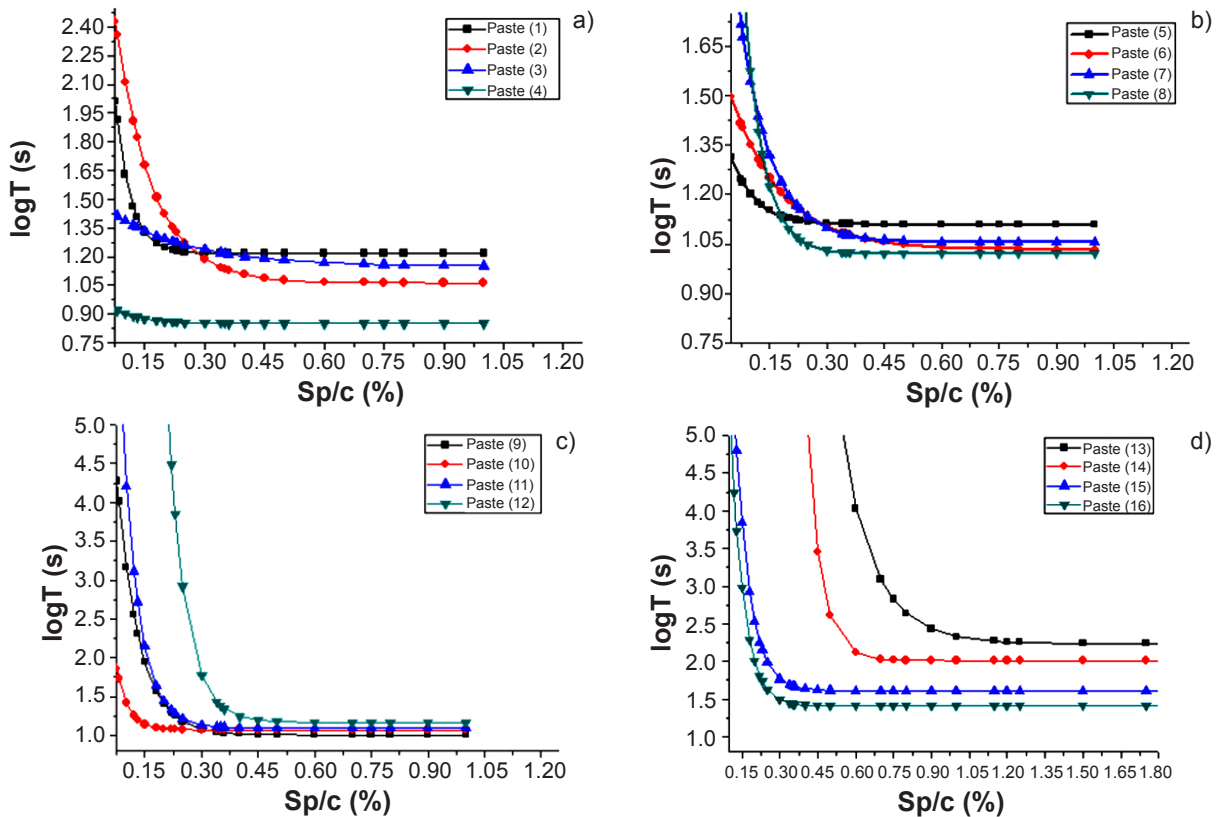


Figure 9: Curves defined by PAM of paste tests 1 to 16.
 [Figure 9: Curvas definidas pelo MAP dos ensaios das pastas 1 a 16.]

Table VIII - Parameters of the flow curves by PAM to different cementitious materials.

[Tabela VIII - Parâmetros das curvas de escoamento determinado pelo MAP para diferentes materiais cimentícios.]

Paste	A_1 (s)	t_1 (%)	y_0 (s)	r^2
1	5.716	0.038	1.217	0.998
2	3.033	0.094	1.062	0.999
3	0.395	0.196	1.150	0.995
4	0.206	0.073	0.850	0.999
5	0.446	0.064	1.109	0.999
6	0.674	0.133	1.033	0.969
7	1.650	0.082	1.055	0.999
8	4.081	0.050	1.021	0.992
9	11.423	0.060	1.006	0.968
10	8.753	0.031	1.072	0.995
11	27.444	0.046	1.093	0.999
12	357.620	0.047	1.168	0.985
13	157.957	0.124	2.241	0.982
14	3880.060	0.057	2.012	0.989
15	32.570	0.056	1.612	0.979
16	29.821	0.051	1.408	0.998

generated doubts in the definition using the other geometric methods. It was observed that the SPS values obtained by AFREM De Larrard [7] were generally higher than those determined by the other methods. This occurred because the AFREM De Larrard method [7] indicated for the SPS a tangency point to the nearest flow curve from the horizontal asymptote. It was noteworthy that for some curves equal values of SPS could be identified using different geometric methods.

CONCLUSIONS

The paste fluidity tests of cement matrices using the Marsh cone are simple and fast, providing identification parameters of the paste quality for using in SCC, HPC and pumpable concretes. The existing methods for determining the saturation point of superplasticizer (SPS) were used successfully, however, they had some limitations. In general, the existing methods propose dosing intervals. According to the results obtained by proposed analytical method (PAM), it was verified that it is possible to establish an equation that characterizes the phenomenon of the Marsh cone flow, correlating the percentage of superplasticizer to cement ratio - SP/c (x-axis), and the decimal logarithm of flow time, logT (y-axis). The Aïtcin method, although is

Table IX - Results of SPS values defined by different methods - SP/c (%).

[Tabela IX - Resultados dos valores de PSP definidos por diferentes métodos - SP/c (%).]

Paste	Differential equation	PAM	Gomes [10]	ASTM C939 [18]	AFREM De Larrard [7]
1	$\frac{dy}{dx} = -149.336.e^{-26.126.x} = -0.57$	0.21	0.25	0.25	0.35
2	$\frac{dy}{dx} = -32.004.e^{-10.552.x} = -0.57$	0.38	0.60	0.60	0.60
3	$\frac{dy}{dx} = -2.007.e^{-5.081.x} = -0.57$	0.24	0.30	0.30	0.35
4	$\frac{dy}{dx} = -2.829.e^{-13.734.x} = -0.57$	0.12	0.15	0.20	0.20
5	$\frac{dy}{dx} = -0.446.e^{-15.455.x} = -0.57$	0.18	0.20	0.20	0.20
6	$\frac{dy}{dx} = -0.674.e^{-7.518.x} = -0.57$	0.33	0.10	0.20	0.35
7	$\frac{dy}{dx} = -1.650.e^{-12.195.x} = -0.57$	0.32	0.25	0.25	0.35
8	$\frac{dy}{dx} = -4.081.e^{-20.000.x} = -0.57$	0.26	nd	0.20	0.30
9	$\frac{dy}{dx} = -188.76.e^{-16.528.x} = -0.57$	0.37	nd	0.25	0.35
10	$\frac{dy}{dx} = -282.354.e^{-32.258.x} = -0.57$	0.20	0.12	0.12	0.12
11	$\frac{dy}{dx} = -596.608.e^{-21.739.x} = -0.57$	0.33	0.25	0.25	0.35
12	$\frac{dy}{dx} = -7774.347.e^{-21.739.x} = -0.57$	0.45	0.35	0.35	0.55
13	$\frac{dy}{dx} = -1273.79.e^{-8.064.x} = -0.57$	0.95	nd	1.50	1.50
14	$\frac{dy}{dx} = -68071.22.e^{-17.543.x} = -0.57$	0.66	0.70	0.70	0.80
15	$\frac{dy}{dx} = -707.815.e^{-18.518.x} = -0.57$	0.38	0.40	0.45	0.45
16	$\frac{dy}{dx} = -68071.22.e^{-17.543.x} = -0.57$	0.35	0.30	0.30	0.40

nd - not defined (angle not found with test data).

advantageous to verify the paste workability, presents a longer time of execution than the others. In addition, its use may not be possible when there is an incompatibility between the cementitious materials and SP. The methods of Gomes and AFREN, as well as the ASTM C939, need visual and geometric resources, which may hinder an accurate SPS identification or turns it impossible to be determined. On the other hand, the decreasing exponential defines adequately the flow behavior of cementitious materials using the Marsh cone. It was verified that PAM provides a satisfactory result to define the SP's optimum point, improving the accuracy of SPS reference value. Moreover, PAM allows a numerical model implementation and may be part of a programmable model for the concrete dosage.

ACKNOWLEDGMENTS

The authors thank LEMA, CTEC, UFAL, PPG Materials, CAPES, CNPq and FAPEAL, for their support to the study.

REFERENCES

- [1] H. Okamura, *Concr. Int.* **19**, 7 (1997) 50.
 [2] P.K. Mehta, P.J.M. Monteiro, *Concreto: microestrutura, propriedades e materiais*, Ibracon, S. Paulo (2008).
 [3] A.M. Neville, J.J. Brooks, *Tecnologia do concreto*, 2^a ed., Bookman, Porto Alegre (2013).
 [4] R. Gettu, J. Roncero, P.C.C. Gomes, in 42^o Congr. Bras. Concr., Recife (2000).
 [5] K.A. Melo, A.M.P. Carneiro, *Constr. Build. Mater.* **24**, 8 (2010) 1529.
 [6] P.C. Aïtcin, *Constr. Build. Mater.* **9**, 1 (1995) 13.
 [7] F. De Larrard, F. Bosc, C. Catherine, F. Deflorenne, *Mater. Struct.* **30** (1997) 439.
 [8] J. Roncero, "Effect of superplasticizers on the behavior of concrete in the fresh and hardened states: implications for high performance concretes", Dr. Thesis, Un. Polit. Cataluña, Barcelona (2000).
 [9] C. Chakkamalath, R. Gettu, *Mater. Struct.* **41** (2008) 1581.
 [10] P.C.C. Gomes, R. Gettu, L.A. Fité, C. Bernad, *Cem. Hormigón* **832** (2002) 30.
 [11] B. Toralles-Carbonari, R. Gettu, L.A. Fité, A. Aguado, *Cem. Hormigón* **774** (1997) 932.
 [12] E. Jhon, R. Gettu, *ACI Mater. J.* **111**, 1 (2014) 67.
 [13] P.F.G. Banfill, *Mag. Concr. Res.* **33**, 114 (1981) 37.
 [14] R.G. Pileggi, F.A.C. Betioli, V.M. John, in Proc. 12th Int. Congr. Chem. Cem., Montreal (2007).
 [15] D.L. Kantro, *Cem. Concr. Compos.* **2** (1980) 95.
 [16] P.C. Aïtcin, C. Jolicoeur, J.G. Macgregor, *Concr. Int.* **16**, 5 (1994) 45.
 [17] L. Agulló, B. Toralles-Carbonari, R. Gettu, A. Aguado, *Mater. Struct.* **32** (1999) 479.
 [18] ASTM C939-10, "Standard test method for flow of grout (flow cone method)" (2010).
 [19] D.C. Montgomery, C.G. Runger, *Applied statistics and probability for engineers*, 5th ed., John Wiley Sons, USA (2011).
 (Rec. 17/10/2018, Rev. 07/01/2019, Ac. 08/01/2019)

