



The 7th World Congress on Particle Technology (WCPT7)

## Correlating aggregates structure with PEL characteristics using an experimental design methodology

Maria G. Rasteiro<sup>a\*</sup>, Ineide Pinheiro<sup>a</sup>, Paulo J. Ferreira<sup>a</sup>, Fernando A. Garcia<sup>a</sup>, Christine Wandrey<sup>b</sup>, Hamideh Ahmadloo<sup>b</sup>, David Hunkeler<sup>c</sup>

<sup>a</sup> Centre for Chemical Process Engineering and Forest Products, Chemical Engineering Department, University of Coimbra, Portugal

<sup>b</sup> École Polytechnique Fédérale de Lausanne, Switzerland

<sup>c</sup> Aqua+ Tech, Switzerland

### Abstract

Aggregation of particles is fundamental for improving the performance of many solid/liquid processes. Aggregation can be induced by different means, one of the most common being based on the addition of polymeric additives, namely polyelectrolytes (PEL). In this work we have studied the flocculation of precipitated calcium carbonate (PCC), used as filler in papermaking, induced by a range of cationic polyacrylamides with different structures, varying in molar mass and degree of branching. The flocculation process was monitored continuously using the LDS technique. Using an experimental design strategy it was possible to produce a model which allows us to relate the aggregates structure, described by the scattering exponent (SE), with the PEL characteristics and concentration ( $R^2$  around 79%). The Partial Least Squares (PLS) regression method was selected to perform the regression, given the significant collinearity among the input variables. The results obtained lead us to conclude that the polymer intrinsic viscosity (related with the PEL molar mass and charge density, and supplying information about the volume of the polymer molecule in the solution) and the degree of branching, are the parameters with a stronger influence on the resulting flocs structure. The PLS model developed was successfully validated using an independent data set, which provides confidence on its consistency and prediction accuracy.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Selection and peer-review under responsibility of Chinese Society of Particuology, Institute of Process Engineering, Chinese Academy of Sciences (CAS)

**Keywords:** Flocculation; Polyelectrolytes; LDS; Scattering exponent; Partial Least Squares Regression.

\* Corresponding author. Tel.: +351-239-798-700; fax: +351-239-798-703.  
E-mail address: [mgr@eq.uc.pt](mailto:mgr@eq.uc.pt)

## 1. Introduction

Aggregation of particles is fundamental for improving the performance of many solid/liquid processes. Aggregation can be induced by different means, one of the most common being based on the addition of polymeric additives, namely polyelectrolytes (PEL). Flocculation by polyelectrolytes is of importance to many industrial areas, namely in food, pharmaceuticals and also in papermaking.

In the case of papermaking, flocculation is the most important phenomena of the wet-end stage since it affects process efficiency (e.g. retention, drainage and runnability) and the quality of the final product [1]. However, to control the flocculation process it is necessary to know and understand how chemical additives act during the whole process.

Various processes occur simultaneously during flocculation: adsorption of polymer molecules at the particles surface; re-arrangement (or re-conformation) of adsorbed polymeric chains; collisions between destabilized particles to form aggregates (flocs); and break-up of flocs. The importance of each process depends on the flocculant characteristics, like structure, molar mass, charge density and concentration; on the characteristics of the suspended particles, like size and charge; on the characteristics of the suspending medium, like conductivity and ionic charge; and, finally, on the contact time and turbulence intensity.

The structure of the polyelectrolyte determines its conformation when adsorbed on the particle surface and, therefore, the predominant flocculation mechanism [2]. In general, if molar mass is high and charge density is low the polymer adsorbs on the particle surface in such a way that it extends beyond the electric double layer and can interact with the polymer adsorbed on other particles – in this case the flocculation process is dominated by bridging bonds [3,4]. When the charge density is high, the bridging capability is reduced because there is a tendency for the polymer chains to adopt a flatter conformation on the particle surface, which results in the formation of patches that attract the polymer free surfaces of other particles [4]. On the other hand, the introduction of branches in the polymer chain can alter the PEL conformation on the particle surface and influence the aggregation mechanism.

The concentration of the flocculant can also be an important parameter, since the rate of adsorption depends on the amount of polymer per unit area of the particle surface. Moreover, the flocculant concentration also affects the re-conformation rate of PEL: polymer re-arrangement is relatively fast at low surface concentration but rather slow on crowded surfaces since neighbouring molecules interfere with the re-arrangement [3, 5].

In this work we have studied the flocculation of precipitated calcium carbonate (PCC), used as filler in papermaking, induced by a range of cationic polyacrylamides with different structures, varying in molar mass and degree of branching. The particles have been kept constant (PCC particles with a median diameter of 2.05  $\mu\text{m}$  and surface potential - 32mV) and all tests were conducted in distilled water. The flocculation process was monitored continuously using the LDS technique (laser diffraction spectroscopy) [6], which provides information about the size distribution and structure (fractal dimension and scattering exponent) of the aggregates [3,7], for each sampling instant and, thus, about the whole kinetics of the flocculation process.

All this information must be treated adequately, in order to better understand the effect of the different parameters, referred above, on the flocculation process. In a previous study [8], we have evaluated how the PEL characteristics and concentration affect flocculation efficiency. Here, since the aggregates structure, namely the flocs compactness, is an important characteristic which may condition the aggregates performance, including their resistance, dewatering ability, sedimentation, etc, and, as a consequence, the final application of the aggregates produced, we have used the experimental information obtained to analyse how the PEL characteristics affect the aggregates structure.

Using an experimental design strategy it was possible to produce a model which allows us to relate the aggregates structure, described by the scattering exponent, SE (related to the secondary aggregates structure), with the PEL characteristics and concentration ( $R^2$  around 79%). The Partial Least Squares (PLS) regression method was selected to perform the regression, given the significant collinearity among the input variables. Unlike Ordinary Least Squares (OLS), PLS effectively handles situations where the X-variables (or input variables) are highly collinear, as happens in the present situation [9,10]. It basically consists in finding a lower dimensional subspace of the whole X-variables hyperspace, which presents a high covariance with the response and also provides a proper description of the original X data. By first projecting the X-variables observations onto such a predictive subspace, and using the

result of such operation as the new predictor variables, one can effectively handle the correlation structure present, and obtain a stable and robust predictive model.

## 2. Experimental

### 2.1. Materials

In this work, we have used nine cationic polyacrylamides (C-PAM) emulsions of different molecular weight with a charge density between 40 and 50% (w/w), copolymers of acrylamide (AM) and acryloyloxyethyltrimethyl ammonium chloride, developed and supplied by AQUA+TECH [11,12]. The main characteristics of the polyelectrolytes are summarized in Table 1. Flocculant solutions were prepared with distilled water at 0.1% (w/w).

The flocculation tests were carried out on a commercial scalenohedral PCC suspension, supplied by OMYA. The PCC suspension was prepared at 1% (w/w) in distilled water. The median size of the particles was approximately 2.05  $\mu\text{m}$  (measured by LDS) and the suspension pH, 8.5. The zeta potential of the particles was -32 mV in distilled water.

### 2.2. Experimental techniques

The intrinsic viscosity (IV) is a suitable and informative parameter, in particular when the goal is the assessment of the impact of PEL of different chain architectures and structure on technological processes where the polymer coil dimensions are important. For a known molar mass, the polymer coil size in solution depends upon the chemical structure, chain architecture (linear, branched), and the solvent quality. IV is dependent on the coil size of the polymer in solution and, thus, can supply information about the conformation adopted by the PEL in solution.

The IV of the isolated and redissolved copolymers was determined in 0.05 M NaCl aqueous solution at  $20 \pm 0.1^\circ\text{C}$  by dilution viscometry, using an automatic capillary viscometer, Viscologic T11 (Semantech, France). The extrapolation to zero concentration was performed according to Huggins' method [13]. Table 1 summarizes the properties of the polymers tested.

Table 1. Summary of the flocculants characteristics.

Alpine Flocc <sup>TM</sup>	Intrinsic viscosity – IV (ml/g)	Charge density (w/w %)	Number of branches
E1	2308	45.5	0
E1+	1817	48.8	1
E1++	1771	46.6	2
E1++++	1775	42.8	4
E2	1550	47.3	0
E2+	1164	41.4	1
E2++++	977	42.1	4
E3	989	44.6	0
E3++++	594	40.1	4

PCC flocculation was monitored by measuring the aggregates size using light diffraction spectroscopy (LDS) in a Malvern Masterziser 2000 (Malvern Instruments). The PCC suspension was added to 700 mL of distilled water in the equipment dispersion unit, until a certain, fixed level of obscuration was obtained, corresponding to an average

PCC concentration around 0.05% (w/w). The tests were carried out with stirring and in turbulent conditions (1400 rpm corresponding to an average shear rate of 312 s<sup>-1</sup>) as described elsewhere [6].

Flocculants were tested for a range of concentrations, usually close to the optimum dosage, which is defined as the PEL dosage leading to larger flocs and fastest kinetics.

To determine the flocculation kinetics curve, a predetermined amount of flocculant was added at once to the suspension and the flocs size distribution was measured every minute during 14 minutes, i.e., until the flocs size stabilized.

Fig. 1 gives two examples of the flocculation kinetic curves obtained for the flocculation of PCC with E1 and E2. It is obvious from the analysis of Figure 1 that the shape of the kinetic curve depends on the polyelectrolyte characteristics. For the lower molar mass polymer (E2) there is no reformation of the aggregates, after reaching the maximum floc size, the opposite happening for the high molar mass polymer (E1). Moreover, the flocculation rate, during the first stage of flocculation, is faster with the higher molar mass polymer (E1). The experimental flocculation results corresponding to the range of polymers in Table 1 have been presented in detail elsewhere [7].

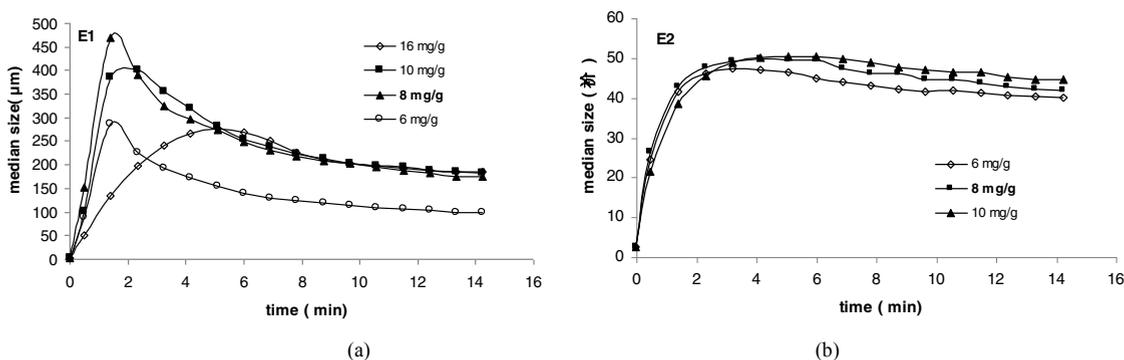


Fig. 1. Flocculation kinetic curves obtained with LDS: flocculation of PCC induced by E1 (a) and E2 (b).

From the scattering matrix produced by the LDS technique it is also possible to extract information about the fractal dimension of the aggregates. By plotting, in logarithmic scale, the scattering intensity versus  $q$  ( $q=4\pi n_0/\lambda_0 \sin(\theta/2)$ ), where  $n_0$  is the refractive index of the dispersing medium,  $\theta$  the scattering angle and  $\lambda_0$  the incident light wavelength, the slope of the decay region is related to the fractal dimension of the aggregates [3,7]. When both primary and secondary aggregates are simultaneously present in the flocs, two regions with different slopes can be identified in the scattering plot (Fig. 2). Region 1, corresponding to the larger length scales (smaller angles), is related to the secondary aggregates and characterized by the scattering exponent (SE). Region 2, corresponding to the smaller length scales (larger angles), is related to the primary aggregates and is characterized by the fractal coefficient ( $d_f$ ).

Mass fractal dimension provides a way of expressing the degree to which primary particles fill the volume of the aggregate:

$$m(R) \propto R^{d_f} \tag{1}$$

where  $m$  is the mass of the aggregate of radius  $R$ .

For solid non-porous particles  $d_f=3$  and for porous particles  $1 < d_f < 3$  [3].

For secondary aggregates, where restructuring has occurred, the fractal theory no longer applies, but information about the flocs structure can be provided by the scattering exponent (SE) which is, in this case, a mere proportionality coefficient between scattering intensity and  $q$ . This coefficient stands for the case of polydisperse aggregates composed of polydisperse particles/primary aggregates, being still related to the structure of the aggregates [3,7]. Therefore, both  $d_f$  and SE can be used to supply information about the aggregates structure, SE being a more adequate parameter to describe the structure of secondary aggregates.

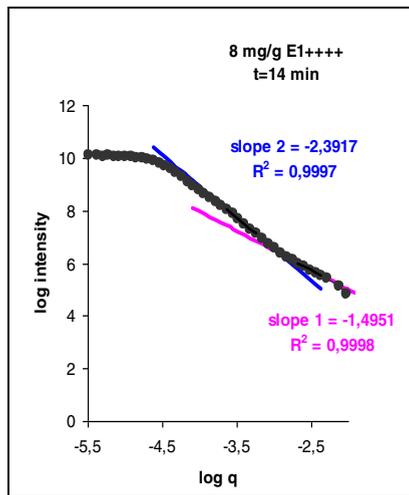


Fig. 2. Scattering pattern of an aggregate.

Fig. 3 gives two examples of how both SE and  $d_F$  evolve with time, during the flocculation process, for two of the polymers studied (E1 and E2).

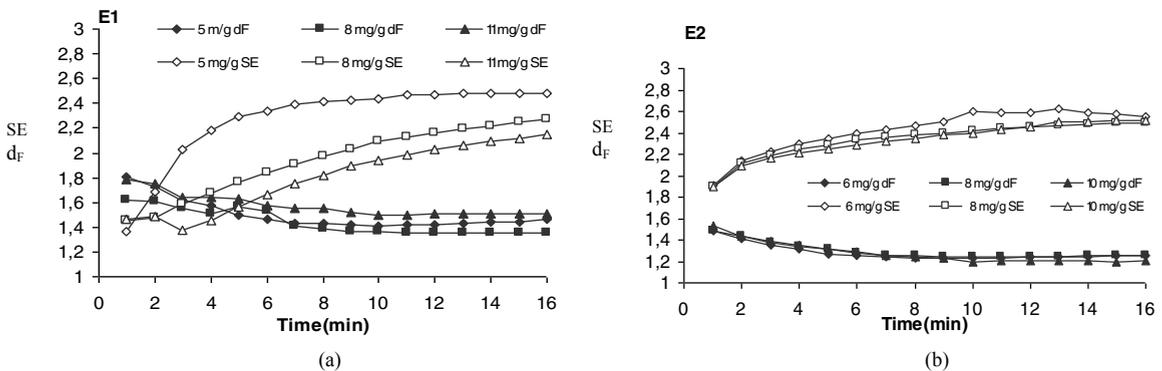


Fig. 3. Evolution of flocs structure with time ( $d_F$  and SE) for E1 (a) and E2 (b).

Analyzing Fig. 3 it is obvious that comparing E1 and E2, for the lower molar mass polymer (E2) the aggregates become more compact (larger SE) straightaway after the beginning of the flocculation process. Additionally, at the end of flocculation these aggregates reach larger values of SE (more compact flocs). It is also apparent in both cases that as flocculation proceeds the aggregates become more compact (SE increases with time).

From the SE profiles obtained for the different polymers tested, we have extracted, for each case, the SE value corresponding to the maximum in the flocculation kinetics curve (larger aggregates diameter). These values are summarized in Table 2. These values will be used in the PLS regression method to perform the regression and obtain the model to predict flocs structure as a function of PEL characteristics.

Table 2. Summary of the experimental SE values for the maximum in the flocculation kinetic curve for the different polymers and concentrations.

Polymer	Concentration (mg PEL/g PCC)	d <sub>50</sub> (µm)	SE
E1	6	230	1.68
E1	8	450	1.48
E1	11	333	1.49
E1+	8	266	1.52
E1+	10	270	1.54
E1+	12	186	1.86
E1++	18	435	1.47
E1++	20	510	1.34
E1++	22	285	1.89
E1++++	8	266	1.40
E1++++	10	281	1.43
E1++++	12	112	1.41
E2	6	41	2.14
E2	8	50	2.19
E2	10	39	2.09
E2	14	42	2.16
E2+	6	96	1.79
E2+	10	135	1.53
E2+	13	79	1.90
E2++++	6	286	1.67
E2++++	8	354	1.53
E2++++	10	282	1.50
E3	2	27	2.07
E3	6	45	1.96
E3	8	34	2.08
E3++++	6	74	1.94
E3++++	10	167	1.74
E3++++	12	190	1.53
E3++++	14	183	1.55

### 3. Partial least squares

Partial least squares (PLS) regression is a method for relating two data matrices, the X-variables or predictors (or input variables), and the Y-variables or responses, through a linear multivariate model. PLS is able to cope with highly collinear predictors, as happens in the present work, being furthermore able to handle noisy and even incomplete data in both predictors and responses [9, 10].

PLS is a bilinear calibration method that finds those linear combinations of predictors presenting maximal covariance with the response. These linear combinations, called latent variables, are found sequentially, each one spanning a different part of the predictive space, until a point where prediction ability does not improve significantly, or begin getting worse.

The PLS model can be re-expressed as a regular regression model, with the same form of one derived from OLS, but with coefficients estimated through the PLS regression algorithm,  $B_{PLS}$ , namely:

$$Y = X \cdot B_{PLS} + F \quad (2)$$

where  $F$  is a residual matrix.

PLS modeling is sensitive to the scale in which variables are expressed. It works better when data are quite symmetrically distributed and have a rather constant error variance. Usually, data are centered and scaled to unit variance before analysis, especially when variables have different units or scales of variability. Scaling all variables to unit variance corresponds to the assumption that all variables are, *a priori*, equally important in the modelling task [14]. In this work, all variables were centred and scaled to unit variance.

### 3.1. Cross-validation

In order to validate the model, two types of approaches can be adopted. The best way is to use an independent data set where the model is applied and its prediction ability assessed (external validation). However, this requires an independent data set, which quite often cannot be provided, as data collected is scarce. In this study we have used external validation to verify the model.

## 4. Results

In the present work, three predictor variables were considered: branching ( $x_1$ ), concentration ( $x_2$ ) and intrinsic viscosity ( $x_3$ ). The response variable is the scattering exponent (SE) for the maximum in the flocculation kinetic curve, and which is a measure of the aggregates structure. These values are summarized in Table 2 for the different polymers and concentration.

The main objective of this study was to identify the most important variables for the relation (SE versus  $x_1, x_2, x_3$ ) and to find the combination of factors describing better the scattering exponent of the aggregates. The PLS methodology was used for that purpose. Every test, for each set of conditions (polymer type and concentration) was repeated at least twice. However, in the PLS regression modelling, each test was considered individually, i.e. the values in the matrix were not the average values of the repetitions, but the individual values for each sample.

Fig. 4 (a) represents the evolution of the model's coefficients of determination versus the number of components of the PLS model, and Fig. 4 (b) corresponds to the predicted response versus the actual response in leave-one-out cross-validation. The vertical line in Fig. 4 (a) indicates that the optimal model has nine components. The response plot (Fig. 4 (b)) indicates that the model predicts the observations quite well. Although there are differences between the fitted and cross-validated fitted, none are severe enough to indicate an extreme leverage point.

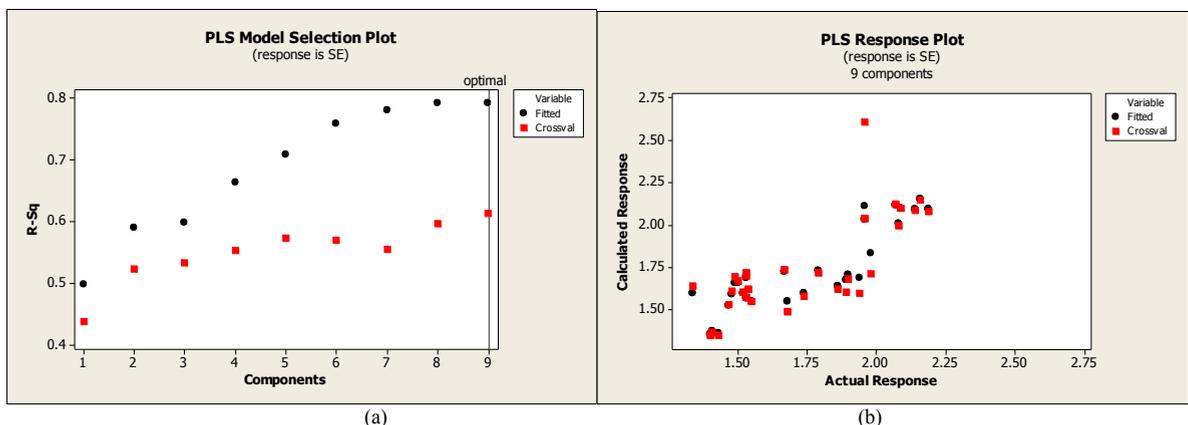


Fig. 4. Evolution of the fitted and cross-validated coefficient of determination with the number of latent variables considered in the PLS model (a) and fit and cross-validated fitted responses for the PLS response (b).

We selected 9 components for analyzing the model, because they are able to explain 79% of the model response, and not much improvement is achieved in the model with further addition of components. The model with 9

components, selected by cross-validation, has a reasonably high  $R^2$  of 79% providing good indicators for its fitting ability and predictive accuracy.

Fig. 5 and Table 3 display the regression coefficients for the scattering exponent (SE) model. Obviously, branching and intrinsic viscosity are the most important factors, but the influence of concentration cannot be neglected. The plot of Fig. 5 can be used to interpret the magnitude and sign of the coefficients. The variables  $x_1$ ,  $x_3$ ,  $x_1 \times x_3$ ,  $x_1 \times x_1$  and  $x_3 \times x_3$  have the largest coefficient and impact on the aggregates scattering exponent model.

Table 3. Coefficients for SE model with 9 components.

	SE	SE standardized
Constant	1.4685	0,000
1- $x_1$	-0.2923	-1.8305
2- $x_2$	-0.051	-0.8655
3- $x_3$	0.0012	2.3551
4- $x_1 \times x_2$	-0.0018	-0.1231
5- $x_1 \times x_3$	-0.00012	-0.9452
6- $x_2 \times x_3$	0.00002	0.6612
7- $x_1 \times x_1$	0.08547	2.2368
8- $x_2 \times x_2$	0.0015	0.6168
9- $x_3 \times x_3$	0,0	-0.8705

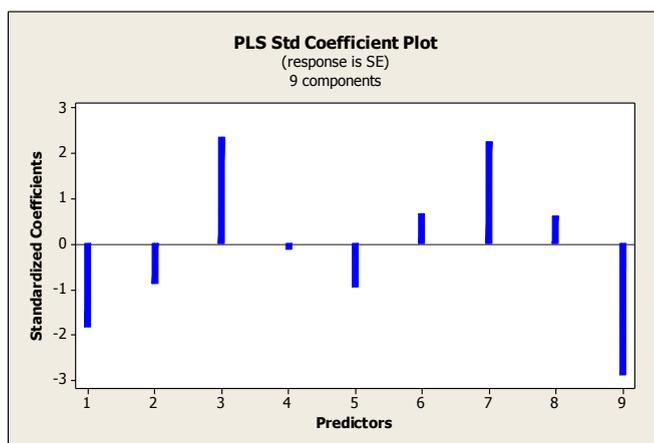


Fig. 5. Standardized PLS coefficients.

#### 4.1. Validation of the PLS model for SE

In order to assess the models consistency and prediction accuracy, an independent test set, never used before during the estimation stage, was collected and used for testing the model developed. This data set constitutes the "F" series of polymers, whose characteristics are summarized in Table 4, comprising a total of 24 new samples.

Table 4. Summary of the flocculants characteristics in the test set.

Alpine Flocc <sup>TM</sup>	Intrinsic viscosity – IV (ml/g)	Charge density (w/w %)	Number of branches
F1	1399	35.0	0
F1+	1144	29.5	1
F1++	687	37.7	2
F1++++	816	34.4	4

Introducing the X-variables for the test set in the model developed, it is possible to obtain their point and interval estimates, which can be compared with the observed values. Of particular importance in this stage is the analysis of the sample-specific prediction intervals (PI), which should contain the observed samples with a given probability, defined *a priori*, through the specification of the confidence level (in the present case, such probability is of 95%).

Table 5 summarizes the results obtained, where it is possible to verify that all samples lay within the prediction intervals. These results confirm the stability and accuracy of the model developed.

Table 5. Validation results for the model for SE developed.

SE_observed	SE_predicted	PI: lower bond	PI: upper bond
2.07	2.00149	1.700544	2.302436
2.07	2.00149	1.700544	2.302436
2.12	2.042252	1.745627	2.338876
2.12	2.042252	1.745627	2.338876
2.02	2.092357	1.792649	2.392065
2.02	2.092357	1.792649	2.392065
1.68	1.739888	1.437155	2.042621
1.68	1.739888	1.437155	2.042621
1.52	1.752457	1.451376	2.053538
1.52	1.752457	1.451376	2.053538
1.41	1.785084	1.482535	2.087633
1.41	1.785084	1.482535	2.087633
1.62	1.557238	1.217394	1.897083
1.62	1.557238	1.217394	1.897083
1.55	1.563122	1.209121	1.917123
1.55	1.563122	1.209121	1.917123
1.45	1.569964	1.20425	1.935679
1.45	1.569964	1.20425	1.935679
1.7	1.635484	1.334013	1.936956
1.7	1.635484	1.334013	1.936956
1.46	1.614942	1.315758	1.914126
1.46	1.614942	1.315758	1.914126
1.35	1.596736	1.29409	1.899382
1.35	1.596736	1.29409	1.899382

Fig. 6 shows the surface plots for the scattering exponent as a function of x1 and x3 (a) and as a function of x1 and x2 (b). From these plots we can conclude that increasing branching (x1) leads to less compact floes and as IV (x3) increases floes become also less compact. Moreover, if concentration (x2) increases floes are in general more compact.

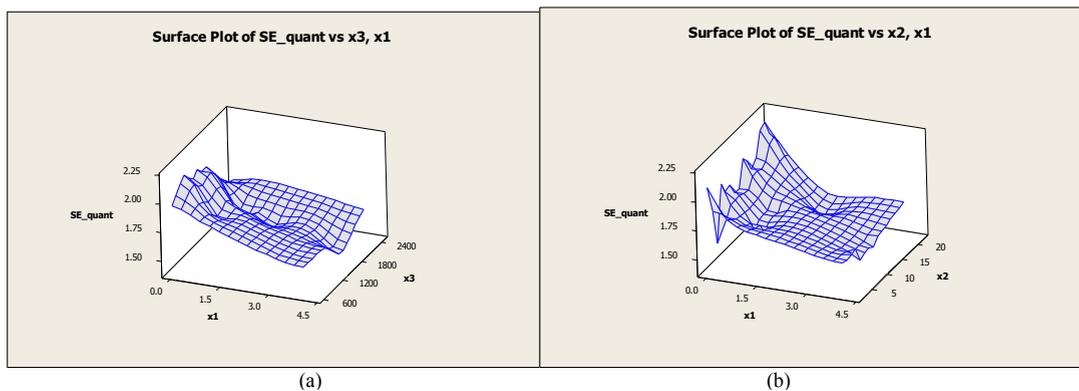


Fig. 6. Surface curves for SE: as a function of x1 and x3 (a) and as a function of x1 and x2 (b).

## 5. Conclusions

Flocculation of precipitated calcium carbonate was monitored using light diffraction spectroscopy. Several cationic polyacrylamides with different molar mass and degree of branching, all copolymers of acrylamide and acryloyloxyethyltrimethyl ammonium chloride, were tested. LDS supplied information about the kinetic curves for flocs growth and about how aggregates structure evolved with time.

A partial least squares (PLS) method was used to identify and correlate the most important variables influencing the aggregates structure. The model could explain quite well the variability observed in the experimental data.

The results obtained lead us to conclude that the polymer intrinsic viscosity (related with the PEL molar mass and charge density, and supplying information about the volume of the polymer molecule in the solution) and the degree of branching, are the parameters with a stronger influence on the flocs structure. The PLS model developed was also successfully validated using an independent data set, which provides confidence on its consistency and prediction accuracy.

For the range of concentrations tested, all close to the optimum concentration leading to the highest flocs size and flocculation rate for each polymer, concentration did not play a very important role on the model, though it could not be neglected.

The same conclusion has been obtained previously when flocculation efficiency, defined as the relation between the maximum flocs size obtained and the time needed to reach it, was correlated with the same polymer characteristics. Thus, it is possible to conclude that the PEL properties most related to the polymer conformation in solution (branching and intrinsic viscosity) exert a stronger influence on both the flocculation efficiency and the flocs structure. For the same type of particles, the polymer conformation in solution defines the way particles interact with each other. The two models available now (for flocculation efficiency and flocs structure) will allow us to better select PEL for specific applications, once we pre-define the flocs structure targeted and the required flocculation efficiency.

## Acknowledgements

The present work was developed under the project PEst/C/EQB/UI0102/2013, financed by FCT/MCTES.

## References

- [1] D. Eklund, T. Lindström, Paper Chemistry: an Introduction, DT Paper Science Publ., Finland, 1991.
- [2] K. E. Bremmell, G. J. Jameson, S. Biggs, Kinetics polyelectrolyte adsorption at the solid/liquid interface interaction forces and stability, *Colloids and Surfaces*, 139 (1998) 199-211.
- [3] S. Biggs, M. Habgood, G. J. Jameson, Yao-de-Yan, Aggregate structures formed via a bridging flocculation mechanism, *Chemical Engineering J.*, 80 (2000) 13-22.
- [4] A. Blanco, E. Fuente, C. Negro, J. Tijero, Flocculation monitoring: focused beam reflectance measurement as a measurement tool *Canadian J. of Chemical Engineering*, 80 (2002) 734-740.
- [5] T. G. M. van de Ven, B. Alince, Heteroflocculation by asymmetric polymer bridging, *J. of Colloid and Interface Science*, 181 (1996) 73-78.
- [6] M. G. Rasteiro, F. A. P. Garcia, P. Ferreira, A. Blanco, C. Negro, E. Antunes, The use of LDS as a tool to evaluate flocculation mechanisms. *Chemical Engineering and Processing*, 47 (2008) 1329-1338.
- [7] M. G. Rasteiro, I. Pinheiro, F. A. P. Garcia, P. Ferreira, D. Hunkeler, Using light scattering to screen PEL performance in flocculation, *Polymers*, 3 (2010) 915-927.
- [8] I. Pinheiro, P. J. Ferreira, F. A. Garcia, M. S. Reis, A. C. Pereira, C. Wandrey, H. Ahmadloo, J. L. Amaral, D. Hunkeler, M. G. Rasteiro, *Powder Technology*, 238, 2-13, 2013.
- [9] H. Martens, T. Naes, *Multivariate Calibration*, Wiley, Chichester, 1989.
- [10] S. Wold, M. Sjostrom, L. T. Eriksson, PLS-regression: a basic tool of chemometrics, *Chemometrics and Intelligent Laboratory Systems*, 58 (2001) 109-130.
- [11] J. Hernandez Barajas, C. Wandrey, D. J. Hunkeler, 2003. U.S. Pat. 6,667,374 B1.
- [12] J. Hernandez Barajas, C. Wandrey, D. J. Hunkeler, 2003. U.S. Pat. 6,617,402 B2.
- [13] L. Bourdillon, D. Hunkeler, C. Wandrey, The analytical ultracentrifuge for the characterization of polydisperse polyelectrolytes. *Progress in Colloid & Polymer Science*, 131 (2006) 141-149.
- [14] S. Wold, M. Sjostrom, L. Eriksson, Partial Least Squares Projections to Latent Structures (PLS) in chemistry. In: P. von Ragué Schleyer (Ed.), *The Encyclopedia of Computational Chemistry*, J. Wiley and Sons, N.Y., 2006-2021, 1998.