Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2017,Volume 8, Issue S, page 4847-4853

http://www.jmaterenvironsci.com

Response surface methodology: A tool for the optimization of the radioactive waste containment matrix

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Received 27 Jul 2017,
Revised 05 Dec 2017,
Accepted 13 Dec 2017

Keywords
- ✓ Radioactive waste,
- ✓ Response surface methodology,
- ✓ Experimental design,
- ✓ Compressive strength,
- ✓ Silica fume,
- ✓ Containment matrix.

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Abstract

The aim of this work is to optimize the operational conditions for the containment matrix of ion exchange resins "IER", considered as a radioactive waste of low and medium activity, generated from the nuclear reactor, using the surface response methodology of experimental design.In order to achieve our objective, we studied the influence of three key parameters (cement content, silica fume content and water/ciment ratio"W/C") on the response studied, which is the compressive strength at long-term of the IER containment matrix. A second-degree polynomial mathematical model was selected to predict the operating conditions that allowed us to optimize the operational conditions of confinement of the IER cementitious matrix while improving its mechanical properties.The obtained results by the selected mathematical model showed that the compressive strength at 28 days of the IER confinement matrix depends only on the linear terms a_2 and quadratic a_{22}/a_{33} relative to the factors: silica fume content, the interaction between silica fume and the interaction between the W/C ratio.At the end of this work, we succeeded to develop a mathematical model to optimizing the most suitable experimental parameters, for the confinement of this type of radioactive waste with a minimum of tests. This model was validated for predicting the compressive strength of this matrix, by playing on the various factors mentioned above.

1. Introduction

The response surface methodology (SRM) by the experimental design is a combination of mathematical/statistical methods and empirical modeling used to improve the performance of processes and products by optimizing operating conditions. The SRM was developed by BOX and Wilson in the late 1940s in the chemical industry [**1**]. It was subsequently applied in numerous process optimization situations in several fields such as chemical processes [**2-5**], geotechnical engineering [**6**], animal science studies and nutrition [**7-9**], agri-food [**10**] and biochemical processes [**11**]. The use of SRM by experimental design allowed the experimenter to determine the number of tests realized in a rational manner, to avoid redundancy of information and to facilitate later time management and cost control. Indeed, the SRM is the only strategy that would truly optimize the overall operational conditions. In other words, it will make it possible to model and optimize the most appropriate conditions for obtaining a better response [**12-16**].

A review of the bibliography shows that the application of this methodology (SRM) in the field of radioactive waste management mainly in containment has not been studied. We were interested in deciding on this aspect in order to optimize the operational conditions of containment matrix of radioactive waste, such as the ion exchange resins (IER) generated from the nuclear reactors.

Following our previous experimental studies on the optimization of confinement matrix used to immobilize the ion exchange resin (IER) as radioactive waste, we have observed that several parameters affected on the physical properties and the mechanical performances of this matrix. Among them the W/C ratio, the nature of the additions (organic/inorganic), the cement content, the mass fraction of ion exchange resin, etc…. [**17-20**]. To study the influence of these parameters, the classical approach often consists in varying a single parameter and measuring its effect on the behavior of the matrix by keeping all the other parameters constant. This approach seems a bit long and produces limited information since the interactions between the parameters of the matrix cannot be evaluated. To remedy, in this study we use the SRM methodology to evaluate the influence of the various parameters and their interactions on the mechanical performance of this matrix.

The choice of this study ranges of different factors (cement X_1, silica fume X_2 and W/C X_3 ratio) was determined from the obtained results by our previous studies [**21**]. The response studied by this approach is the compressive strength at 28 days. Grace of the iso-response curves and/or the response surface, we determined the operational conditions that allowed us to predict the optimal mechanical resistance of compression through a polynomial mathematical model of a second degree.
At the end of this process, a validation test was realized to justify the quality of the chosen model on one hand, and its application on the other hand, while comparing the theoretical results of the compressive strength (calculated from the model) and experimental (retained after application of the optimal conditions obtained by the model).

2. Material and Methods

2.1. Materials

2.1.1. Cement

The type of cement used in this work is a Portland cement with additions (CPJ-45N), its chemical composition obtained by X-ray fluorescenceis presented in the Tables 1.

Table 1: Elementary chemical composition of cement

Composition (%)	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**K_2O**	**Na_2O**
Cement	61.80	19.20	7.80	3.16	2.01	2.40	0.82	0.10

The mineralogical composition of used cement is presented in the Tables 2.

Table 2: Mineralogical composition of clinker

Chemical name	**Mineral name**	**Chemical formula**	**Cement nomenclature**	**Content**
Tricalcium silicate	Alite	Ca_3SiO_5	C_3S	48.69
Dicalcium silicate	Balite	Ca_2SiO_4	C_2S	18.31
Tricalcium aluminate	Aluminate	$Ca_3Al_2O_6$	C_3A	15.32
Tetracalcium Aluminoferrite	Ferrite	$Ca_4Al_2Fe_2O_5$	C_4AF	9.61

2.1.2. Silica fume

The silica fumes are a by-product of the production of silicon and of alloy with Ferro-silicon. Two main effects are recognized: a pozzolanic effect resulting from the amorphous state and a granular effect related to the fineness and the rounded shape of its particles [**22-24**].

The chemical composition of the silica fume used in this work, obtained by X-ray fluorescenceand its physical properties provided by the manufacturer are summarized in Tables (3) and (4).

Table 3: Chemical composition of silica fume

Composition (%)	**CaO**	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**SO_3**	**K_2O**	**Na_2O**	**Cl^-**	**LOI**
SF	0.46	91.20	0.83	1.68	0.94	0.42	0.93	0.77	0.06	2.71

The quality of a mineral addition is related to its glass content. For this purpose, it is sufficient to calculate, from its chemical composition, the difference between the raw silica and lime (silica-lime) contents. When this difference is less than a threshold value of 34%, the mineral addition does not contain a vitreous phase [**25**]. According to the centesimal chemical compositions in the Table (3), this difference is greater than 34%. This means that the silica fume used contains a very appreciable vitreous phase. Thus the possibility of fixing the lime released by the cement during its hydration and to form additional hydrated calcium silicates (C-S-H gel) according to the following pozzolanic reaction:

$CaO+SiO_2+H_2O$ —> C-S-H (Pozzolanic reaction)

Table 4: Physical Properties of Silica fume

Color	**Morphology**	**Density**
Gray	Spherical Particles	$3.27 g.cm^{-3}$

2.1.3. Ion exchange resin (IER)

The IER used in this work as a solid radioactive waste generated by the nuclear reactor of the nuclear studies center of maâmoura – Morocco is a cross-linked polymer in the form at a base of different

structures (cationic and anionic) (Figure 1). It consists of an assembly of three particle sizes: 0.2% of the grains with a diameter of less than 0.31 mm, 80% of the grains with a diameter of 0.4 mm and 1.00 mm and 3% of the grains with a diameter greater than 1.25 mm.

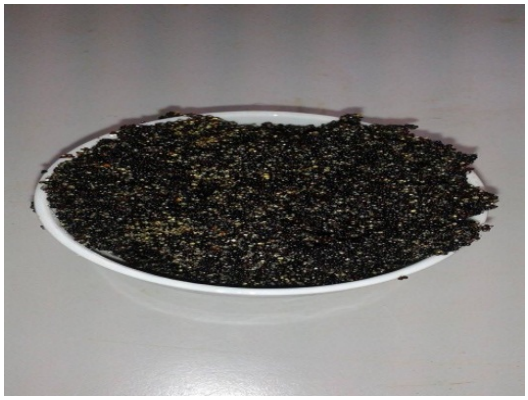

Figure 1: Ion exchange resin - Radioactive waste

2.1.4. Software used

To study the influence of each factor and their interactions on the compressive strength at 28 days of the ion exchange resin confinement matrix, we used the software named : New Efficient Methodology for Research using Optimal Design (NEMRODW). This software allows to optimize the desired process (industrial / research and development), limiting the number of the realize tests (by means of simulations) while improving the quality of the information sought (answer "y").

2.2. Methods

2.2.1. Method of sample preparation

The tested samples are prepared by mixing the cement and the silica fume. By subsequently adding the radioactive waste (ion exchange resins) with a moisture content about of 64%, then spoil our mixture. The resulting mixture is poured into cylindrical molds 5.5 cm in diameter and 10 cm in height previously oiled to facilitate its demolding. These sample tests are then subjected to vibration by a vibrator type Trakita VR 250D to eliminate the air pockets. After a set time, the samples (fig.2) were removed from the mold and kept in a relatively humid room until the crushing time (7d, 4 d, 21d, 28 d and 90 d).

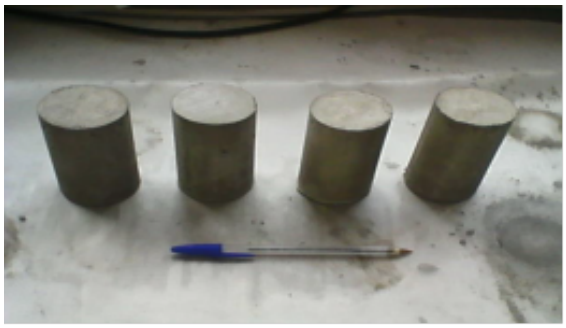

Figure 2: Sample tested

2.2.2. Method of experimental design:

The experimental designs are a part of a general process for improving the quality of the desired process. They allowed us to acquire new knowledge by controlling one or more input parameters at the same time, in order to obtain better results, and validating the selected model, while at the same time minimizing the number of the realized tests, thus saving the time and raw materials in order to optimize the response studied.

2.2.3. Methodology by response surface of experiments design

The aim of the methodology of the response surfaces is to explore the relations between a response (y) and several factors X_1, ..., X_n by fitting a mathematical function (model), graphically representing this function in Space (response surface / iso-response). From the graphical representation, we can describe the principal and secondary effect of each factor and their interactions. This allowed us to find the appropriate operating conditions for the optimization of the studied response (y).

3. Results and discussion

3.1. Studied factors

To optimize the formulation of the confinement matrix of the radioactive ion exchange resins based on the different mass fractions of the addition of the silica fume, we chose the most influencing factors on the response studied (compressive strength at 28 days of curing) which are the cement content (X_1), the silica fume content (X_2) and the water/cement "W/C" ratio (X_3).The tables (5 and 6) present the experimental domain of the studied factors, their experimental matrix and its experimental design that are adopted in our study.

Table 5: Experimental domain

Factor	symbol	Level (+)	Level (-)	Unity	Centre
Cement content (C)	X_1	67.92	57.92	%	62.92
Silica fume content (SF)	X_2	10.00	2.00	%	5.00
(W/C) ratio	X_3	0.30	0.36		0.33

Table 6: Experimental protocol

N° of test	X1=C		X2= SF		X3=W/C		Rcm
	%		%		-		MPa
1	-1	57.92	-1	0.00	-1	0.30	14.60
2	1	67.92	-1	0.00	-1	0.30	14.60
3	-1	57.92	1	10.00	-1	0.30	18.92
4	1	67.92	1	10.00	-1	0.30	18.64
5	-1	57.92	-1	0.00	1	0.36	15.92
6	1	67.92	-1	0.00	1	0.36	14.60
7	-1	57.92	1	10.00	1	0.36	18.92
8	1	67.92	1	10.00	1	0.36	18.92
9	-1	57.92	0	5.00	0	0.33	17.05
10	1	67.92	0	5.00	0	0.33	17.05
11	0	62.92	-1	0.00	0	0.33	14.61
12	0	62.92	1	10.00	0	0.33	17.05
13	0	62.92	0	5.00	-1	0.30	18.17
14	0	62.92	0	5.00	1	0.36	18.64
15	0	62.92	0	5.00	0	0.33	17.05

3.2. Model equation

A quadratic and interaction model (equation 1) was used to predict the main effects (X_i), the secondary effects (X_i^2) and the interaction effects (X_iX_j) between the different factors on the response.

$$\mathbf{Y_{28d} = \partial_0 + \sum_{i=1}^{n} \partial_i X_i + \sum_{i=1}^{n} \partial_{ii} X_i^2 + \sum_{i=1}^{n-1} \partial_{ij} X_i X_j} \quad \text{Equation 1}$$

With Y_{28d} : The compressive strength at 28 days; ∂_0: Constant; ∂i: Regression coefficients of linear effects;∂ii: Regression coefficients of quadratic effects and Xi et Xj: Coded experimental variables

3.3. Statistic study

3.3.1. Estimation and statistics of coefficients

The quality of a model compared to the measured responses is evaluated by the R^2 ratio (Multiple Correlation Coefficient), which represents the ratio of variance explained by the model or due to regression (SCR) and total variance (SCT), Equation 2.

$$R^2 = \frac{SCR}{SCT} \quad \text{Equation 2}$$

More the value of R^2 is near 1, more the model retained explains all the responses measured.

The table 8 presents the estimates and statistics of the model coefficients

From the figure (3) and the table (8), the multiple correlation coefficient $R^2 = 0.970$ and adjustment coefficients $R^{2a} = 0.915$ are sufficient because they have similar values of 1. These values provide good compatibility between the experimental values and those predicted by the adapted model.

The table 9 summarizes the coefficients of all the factors studied, their effects and their statistical values (t-student).

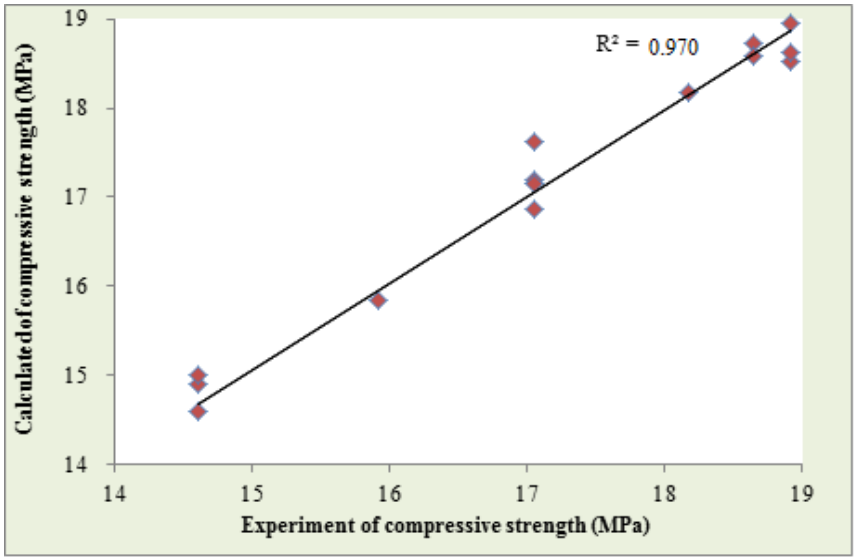

Figure 3: Comparative between theoretical and experimental results

Table 7: Estimates and statistics of the model coefficients

Standard deviation of response	0.505
R^2	0.970
R^{2a}	0.915
R^2 pred	0.613
PRESS	16.231
Number of degrees of freedom	5
R^{2a}: Adjustment coefficient **R^2 pred:** Predictive squares coefficient **PRESS:** Predicted Residual Sum of Squares	

Table 8: Statistical estimation of model coefficients

Term	Coefficients	Estimated value	F.Inflation	t-student	Signif. %
Constant	a_0	17.15		63.14	< 0.01 ***
Cement content	a_1	-0.16	1.00	-1.00	36.5 ns
Silica fume content	a_2	1.81	1.00	11.34	0.0255 ***
W/C ratio	a_3	0.21	1.00	1.29	25.2 ns
Cement content : Cement content	a_{11}	-0.13	1.30	-0.42	69.4 ns
Silica fume content :Silica fume content	a_{22}	-1.35	1.30	-4.29	0.840 **
W/C ratio : W/C ratio	a_{33}	1.22	1.30	3.88	1.21*
Cement content : Silica fume content	a_{12}	0.13	1.00	0.73	50.4 ns
Teneur en ciment : W/C ratio	a_{13}	-0.13	1.00	-0.73	50.4 ns
Silica fume content : W/C ratio	a_{23}	-0.13	1.00	-0.73	50.4 ns
***: Highly significant	**: Very significant		*: Significant		Ns:Not significant

According to the table (9), this shows the different coefficients of the selected model. The value of the inflation factor which is an absolute measure of the independence of the coefficients is near to 1. This shows that the experiment matrix of our study provides desired information. The interest of t-student coefficient is the determination of the significance of the coefficients of each factor. In general, the larger the absolute value of t-student, the more significant the factor [26-29]. From this table, the statistically significant coefficients are a_0, a_2, a_{22}, and a_{33}.

3.4. Graphical analysis of model

3.4.1. Response surface curves and iso-response

The curves of the response surface represent the regression area from a graph in a three-dimensional space. The horizontal plane of this curve presents the domain of variation of 2 factors; the vertical axis represented the variation of the response from the model. While the iso-response curves constitute a projection of the response

surface in the horizontal plane. As with the response surfaces, this representation involves only two factors at a time. The others must be fixed at a constant level [30].
The figure (4) represents the response surface and is-response curves, the significant effects of the factors and their interactions in the measured response, which is the mechanical resistance to compression at 28 days given in MPa.

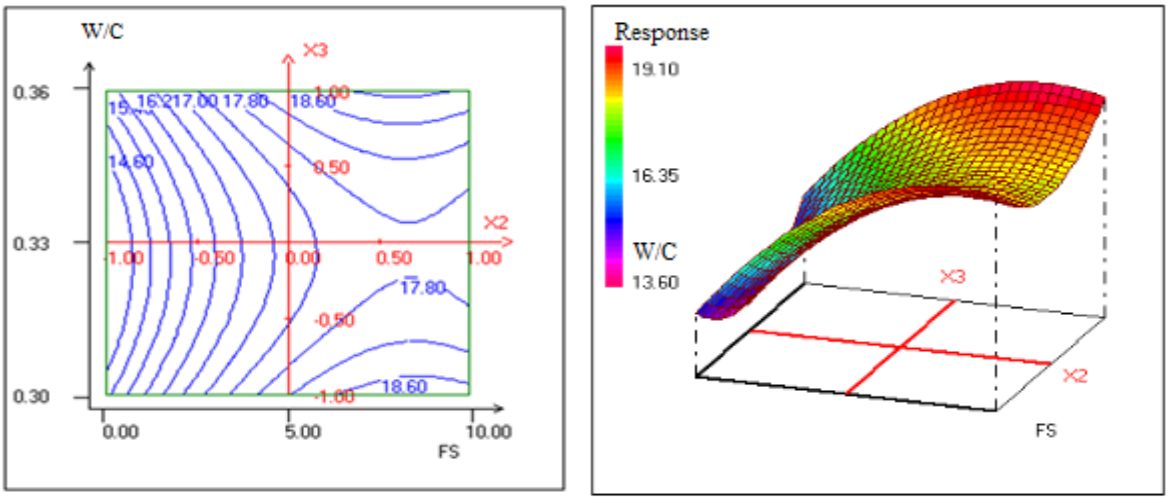

Figure 4: Variation of the compressive strength in the plane: W/C ratio, silica fume content with cement content = 62.92%

From the figure (4), we see growth response curves; in the plane: W/C ratio (X_3) and silica fume content (X_2) and the cement content = 62.92% was fixed; When the W/C ratio increases from 0.30 to 0.36 and the silica fume content is high. Indeed, the compressive strength reaches the maximum when the W/C ratio goes to a higher level and the proportion of the silica fume is high.
From the results of response surface curves and iso-response curves, we have extracted the conditions necessary for the containment matrix of ion exchange resins. They present the optimum of the compressive strength of the cementitious matrix. These conditions are summarized in Table (10).

Table 9: Optimal formulation of the IER containment matrix

Factor	Cement content %	Silica fume content %	W/C ratio
value	62.92	10.00	0.36

3.4.2. Search for the optimum

The mathematical model adapted to the studied response is written in the equation (3), for monitoring the compressive strength of the IER confinement matrix. The factors of the models are linear (X_1, X_2, and X_3), quadratic (X_{12}, X_{22}, X_{32}) and with interaction (X_1X_2, X_2X_3, X_1X_3).

$$Y_{28d} = 17.15 - 0.160 * X_1 + 1.812 * X_2 + 0.207 * X3 - 0.131 * (X_1)^2 - 1.351 * (X_2)^2 + 1.224 * (X_3)^2 + 0.130 * (X_1*X_2) - 0.130 * (X_1*X_3) - 0.130 * (X_2*X_3) \quad \text{Equation (3)}$$

3.5. Selected model

From the table (9) and the figure (4), the compressive strength depends only on the linear factor (X_2) and the quadratic factor $(X_2)^2$ and $(X_3)^2$. Thus, the equation of the mathematical model adopted becomes as follows (Equation 4):

$$Y_{28d} = 17.15 + 1.81 * X_2 - 1.351 * (X_2)^2 + 1.22 * (X_3)^2 \quad \text{Equation (4)}$$

3.6. Model validation

The main objective of our study is to optimize the formulation of the confinement matrix of ion exchange resins based on different percentages of silica fume while minimizing the number of tests performed. To this effect, a validation test of the selected model is necessary to evaluate the effect of the selected factors (cement content, silica fume content and W/C ratio) on the response studied taking into account the optimum conditions given by the selected model: X_1 = 62.92%, X_2 = 10% and X_3 = 0.36 (table 5).
Table 11 shows the values of the predicted and experimental of the compression strength (applying the experimental conditions given by the model).According to the table (11), the predicted and the experimental values of the compressive strength are similar. So, there is no significant difference between the experimental and the predicted responses, which show that the approach used in this study gave us satisfactory results.

Table 10: Predicted and experimental values of the compressive strength at 28 days

Factor	Real value	Coded value	predicted response (MPa)	Experimental response (MPa)
Silica fume content	**10.00**	**1**	18.83	**18.95**
W/C ratio	**0.36**	**1**		

Conclusion

In order to optimize the formulation of the containment matrix of radioactive waste (ion exchange resins), the surface response methodology (RSM) was performed. This approach helps the experimenter to structure his research and to validate his own hypotheses with a minimum of tests. After an appropriate choice of three variables (factors), a mathematical polynomial model of the second degree has been selected.It predicts the factors influencing the response studied (mechanical compressive strength at 28 days).

According to this model, the mechanical compressive strength of the confinement matrix of IER depends only on the linear terms a_2 and quadratic a_{22}/a_{33} relative to the factors: silica fume content, the interaction silica fume content and the optimal values of these factors are therefore the silica fume content = 10%, the W/C ratio = 0.36.

This approach (SRM) allowed us to optimize the most suitable experimental parameters for the confinement of IER with a minimum of tests, while improving the mechanical performance of the confinement matrix of radioactive resins.

References

1. G.E.P. Box, K.B. Wilson, J. Roy,*Stat. Soc. Tome Series B 13*. (1951) 1–45.
2. K. Ravikuma, S. Ramalingam, S. Krishnan, K. Balu, *Dyes. Pigm*. 70 (2006) 18-26.
3. J.C. Echeverra, I. Zarrang, J. Estella, J.J. Garrido, *Appl.Clay. Sci.* 30 (2005) 103-105.
4. E. Sayon,*Chem. Eng. J.* 115 (2006) 213-218.
5. A. Kamoun, B. Samet, J. Bouaziz, M. Chaâbouni, *Analusis*. 27 (1999) 91-96.
6. N. Zangeneh, A. Azizian, L. Lye, R. Popescu,*55th Canad. Soc. Geot. Confer. Ham. Ontar*. 2002.
7. W.B. Roush, R.G. Petersen, G.H. Arscott,*Poultry Sci.* 58 (1979) 1504-1513.
8. M. Toyomizu, Y. Akiba, M. Horiguchi, T. Matsumuto, *J. Nutr*. 112 (1982) 886-896.
9. M. Toyomizu, S. Kimura, Y. Tomita,*Anim. Prod*. 56 (1993) 251-259.
10. H.N. Sin, S. Yusof, N.S. Abdul Hamid, R. y .Abd Rahman,*J. Food Eng*. 73 (2006) 313-319.
11. L. Rodrigues, J. Teixeira, R. Oliveira,*Proce Biochem*.41 (2006) 1-10.
12. K. Gaiser, P. Erickson, P. Stroeve, *J. P.* Delplanque*, Ren. Energy*. 85 (2016) 406-418.
13. S. Ghafari, H. A. Aziz, M. H. Isa, A. A. Zinatizadeh, *J. Haz. Mater*. 163.2 (2009) 650-656.
14. S. S. Moghaddam, M. A. Moghaddam, M. Arami, *J. Haz. Mater*. 175.1 (2010) 651-657.
15. M. Fadil, A. Farah, B. Ihssane, T. Haloui, S. Rachid, *J. Mater. Environ. Sci*. 6.8 (2015) 2346-2357.
16. S. Merabet, A. Bouzaza, M Bouhelassa., D. Wolbert, *J. Wat. Sci*. 22.4 (2009) 565-573.
17. B.El Hilal, L. T. El Allioui, A. Bouih, A. Bekhta, A. El harfi, *Proceedings G-Environ.* 5.3 (2013) 216-222.
18. B.El Hilal, L. T. El Allioui, A. Bouih, A. Bekhta, A. El harfi, *J. Mater. Environ Sci*. 6.4 (2015) 969-976.
19. B.El Hilal, L. T. El Allioui, A. Bouih, A. Bekhta, A. El harfi, *Inter. J. Inn. Appl. Stud*.7 (2014) 729-735.
20. B.El Hilal, L. T. El Allioui, A. Bouih, A. M Rafik, A. El harfi, *Mor. J. Chem*. 4.1 (2016) 215-222.
21.B.El Hilal, L. T. El Allioui, A. Bouih, A. El harfi, *J. Mater. Environ Sci*., 9.3 (**2018)xxx-xxx.**
22. F. De Larrard, S Thierry., *Cem. Concr. Res*. 32.11 (2002) 1699-1704.
23.M. Mazloom, A. A. Ramezanianpour, J. J. Brooks, *Cem. Concr. Comp.* 26.4 (2004) 347-357.
24. V. Yogendran, B. W. Langan, M. N. Haque, M. A. Ward, *Mate. J.* 84.2 (1987) 124-129.
25. F. K. Aoual-Benslafa, S. Abdelaziz, K. Djamel, *Afr. Sci. Rev. Inte. Sci. Tech*. 7.2 (2011).
26. R.F. Teo´filo, M.M.C. Ferreira, *Quim. Nova*. 29 (2006) 338.
27. O. Ghorbel-Bellaaj, S. Hajji, I. Younes, M. Chaabouni, M. Nasri, K. Jellouli, *Inter. J. Boil. Macro*. 61 (2013) 243-250.
28. P. G. González, T. Hernández-Quiroz, L. García-González, *Fuel. Proce. Tech*. 127 (2014) 133-139.
29. M. H.R. Khudhair, M. S. Elyoubi, A. Elharfi, *J. Mater. Environ Sci*. 8.6 (2017)1978-1989.
30. F. Rabier, Thèse. *Institut National Polytechnique de Toulouse*. (2007) 144-145.