On the Robustness of a Cement-Based Matrix for the Conditioning of Evaporator Concentrates – 16417

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ABSTRACT

The presented work is research in progress on the robustness of a cement-based matrix designed for the conditioning of evaporator concentrates with highly variable chemical composition. A change in the waste composition can induce significant alteration of the cement-waste form. However, all criteria imposed by the authorities on the immobilized waste need to be met and the processability of all these possible waste compositions has to be guaranteed. Defining a domain of acceptable waste compositions usually requires to investigating many parameters, which results, with classical approaches, in a high number of trials. Design of experiments (DOE) is shown to be a fruitful alternative which enables to keep the total number of runs within reason without compromising the quality of the achieved results. An example is given, showing how a Plackett-Burman design can be used to determine, among all the waste components, those which significantly influence the properties of the cement-waste forms when they vary within the experimental domain of interest.

INTRODUCTION

One common approach to immobilize and stabilize intermediate-level long-lived (ILW-LL) radioactive effluents is their incorporation in a bituminous matrix [1]. In Belgium, this technique was however abandoned at the end of the ’90s. CEA (the French Alternative Energies and Atomic Energy Commission), ONDRAF/NIRAS (the Belgian National Agency for Radioactive Waste and enriched Fissile Materials) and its industrial subsidiary, Belgoprocess, which manages and executes the industrial activities of the agency, are therefore developing an alternative process based on cementation for the conditioning of such radioactive effluents. The investigated effluent mainly results from the cleaning high-level waste storage tanks a the former Eurochemic nuclear fuel reprocessing plant operated from 1966 to 1974. After concentration by evaporation, it should be mixed with a third party waste stream in proportions varying from 0 to 100%. Both streams are acidic and contain elevated concentrations of nitrate, aluminum and sodium ions. Table I gives the expected variations in the composition of the final stream. The values are based on analyses of the historic waste and of previous batches of the yet to be delivered third party waste. All species are assumed to be in their most oxidized state except for organics. Silica is assumed to be originating from sand from the Dessel area. Organics are postulated to be traces of cleaning agents which were used in the facility in the past.

In a previous work [2], a cementitious conditioning formulation was established, taking into account the specifications for grout implementation at an industrial scale and subsequent disposal of the waste packages. The formulation was further improved for passing new waste criteria (Table II), for enhanced durability towards alkali-silica reaction (ASR) and for allowing more acidic waste to be cemented.

TABLE I. Expected domain of composition of the final waste to be cemented. Definition of factors and associated coded variables for the screening study.

Species		Unit	Min	Max	Coded variable	Min	Max
H^+		mmol/L	1308.00	2002.50	X1	-1	+1
Cl^-		mmol/L	0.90	22.22	X2	-1	+1
SO_4^{2-}		mmol/L	0.00	63.61	X3	-1	+1
NO_3^-		mmol/L	3700.00	4815.47	X4	-1	+1
PO_4^{3-}		mmol/L	0.00	33.17	X5	-1	+1
F^-		mmol/L	0.00	54.16	X6	-1	+1
Al^{3+}		mmol/L	250.00	510.00	X7	-1	+1
Ca^{2+}		mmol/L	0.00	106.37	X8	-1	+1
Fe^{3+}		mmol/L	0.00	99.65	X9	-1	+1
Pb^{2+}		mmol/L	0.00	8.97	X10	-1	+1
Minors	**Ce^{3+}**	mmol/L	0.00	4.80	X11	-1	+1
	SiO_2	mmol/L	0.00	13.64			
	Zn^{2+}	mmol/L	0.00	10.44			
	B	mmol/L	0.00	0.66			
	Organics	g/L	0.00	0.26			
Na^+		mmol/l	1000.00	1575.00	-	-	-

This optimization led to a three-step procedure: after concentration, the acidic radioactive waste is pre-treated with technical sodium hydroxide until the pH reaches 12.5 – 13.5, a consecutive resting period of 72 hours is followed by cementation (Table II) of the resulting alkaline sludge.

TABLE II. cementitious composition for ±1L end-product

CEM III/C 32.5 PM ES Calcia Rombas (Blastfurnace slag cement)	801.1 g
Calcareous sand ENGIS 0-4 mm	392.4 g
Sludge with pH adjusted to 12.5-13.5	600.0 mL

Given the complex chemical composition of the waste, strong interactions between the cementitious matrix and some waste components are to be expected. The waste contains retarders of cement setting and hardening, such as nitrates [3], phosphates [4], heavy metals (lead [5], zinc [6]), fluorides and sulfates (for the cement aluminate phases) [7]. On the contrary, calcium chloride [8] and chromium VI [9] are known to accelerate Portland cement hydration. It should be noted however that most available data are relative to each species taken separately from the others. Additional complexity might be expected due to possible synergetic or antagonistic interactions between the species in mixture. Moreover, unexpected concentration effects are sometimes observed. For instance, phosphate ions have been shown to retard cement hydration [10]. A systematic study of the hydration of cement pastes in phosphate-rich solutions (up to 50 g/L) revealed however that the delay increased with the phosphate concentration up to 25 g/L, but then decreased at higher concentrations [4, 11]. In the same way, carbonate ions, which are present in the technical sodium hydroxide used for titration of the waste, are known to have effects ranging from flash set to retardation of set depending on the concentration in which they are added [4]. A variation in the waste composition can thus induce significant alterations on the cementitious matrix. It is thus necessary to define a domain of acceptable waste compositions, guaranteeing that the cement-waste form can be easily implemented and checks the criteria imposed by the authorities (Table III).

This problem can be addressed using a one-factor-at-a-time approach. This method consists in selecting, for each factor, a starting point, and then in successively varying each factor over its range while holding the others constant at the baseline levels. It has however two drawbacks: the number of trials to be performed is high (32 experiments for 16 species if only two levels of variation are considered), and it fails to consider any possible interaction between the factors. This paper presents another approach, based on design of experiments (DOE), which includes two stages. The first one aims at point-

ing out, among all the waste components, those which significantly influence the properties of the cement-waste forms in fresh and hardened state when they vary within the experimental domain of interest. The second stage, a response surface investigation, is focused on the most influential species with the objective to build empirical models enabling to fit and predict the properties of the cement-waste form as a function of their concentrations in the waste. These models can then be used to point out potential waste compositions that would produce cement-waste forms with insufficient quality. This second step is today beyond the scope of this paper and shall be addressed in a follow-up work.

TABLE III. A summary of the criteria imposed to the waste form.

Subject	**requirement**
Waste from	Solid monolith, stable, non-dispersible, without free liquid.
Temperature	The temperature shall not exceed 60 °C (140 °F) except if it is demonstrated by an appropriate test that the formation of delayed ettringite can be excluded. The temperature should never exceed 100 °C (212 °F) at any point in the waste form. The heat output during setting should not produce mechanical stress susceptible to damage the integrity of the waste form or waste package.
Compressive strength	The compressive strength of the waste form shall be at least 8 MPa
Bending strength	The bending strength of the waste form shall be at least 1 MPa
Curing under water	After curing specimen under water during at least 90 days: - - there shall be no alteration of the structure such as e.g. cracks, - - the bending strength shall be at least 1 MPa.
Curing at low temperature	When cured for at least 120 days at temperatures between 0°C (32°F) and 10°C (50°F) : - - there shall be no alteration of the structure like e.g. cracks, - - the bending strength shall be at least 1 MPa.
Bleeding	All bleed water, if any, shall be reabsorbed after setting
Durability	Test specimens of the waste form shall be cured for at least 12 months at 100% R.H. and 38°C (100.4°F). During this curing period, the absence of structural alteration should be checked. After this aging period,: - the bending strength shall exceed 1 MPa, - the absence of pathologies which may damage the matrix shall be checked by microscopic analyses.
This list is not exhaustive, only criteria relevant for this research are mentioned here.	

BASIC PRINCIPLES OF DOE

DOE refers to the process of planning experiments so that appropriate data will be collected and analyzed by statistical methods, thus resulting in valid and objective conclusions [12, 13]. It is based on a sequential procedure. The questions to be addressed in the experiments directly relate to the goal of the study. If the system is new, as in this work, the initial objective is likely to be factor screening, possibly followed by investigation of the main effects and interactions between factors. If the system is mature or

reasonably well understood, the objective may then be to fit and analyze response surfaces in order for instance to perform predictions or optimization.

Selection of the Factors and Experimental Region of Interest

The factors (or variables) which may influence the system are classified as design factors (the variables actually selected for investigation) or held constant factors (variables which may exert some influence on the responses but which are held at a constant level). Once the factors have been chosen, their range of variation must be defined, which determines the experimental domain. Since the factors units are usually inhomogeneous, coded dimensionless variables are defined.

Selection of the Responses

The selected responses, which are often multiple, must be chosen in order to provide useful information about the process under study.

Assumption of empirical Models for the Responses

Next, empirical models are postulated, that is equations derived from the data that express the relationship between responses and factors, mostly polynomials. Their form depends on the objectives of the study. For instance, in the first step of the approach adopted in this work, the *linear model* is used, whereas a quadratic model will be used in the second step:
Linear (screening study):

$$y = \beta_0 + \Sigma_{i=1..n} \beta_i x_i + \varepsilon \quad \text{(eq. 1)}$$

Quadratic (response surface investigation):

$$y = \beta_0 + \Sigma_{i=1..n} \beta_i x_i + \Sigma_{i=1..n-1} \Sigma_{j=i+1...n} \beta_{ij} x_i x_j + \Sigma_{i=1..n} \beta_{ii} x_i^2 + \varepsilon \quad \text{(eq. 2)}$$

where: y is the response value, x_i the level of coded factor X_i, β_i the i^{th} model parameter, and ε the error. It must be clear that these models are on no account phenomenological ones.

Selection of Experimental Design

The positioning of experimental points within the experimental domain is of great importance to obtain a good precision on the estimates of the model parameters and, in the case of response surface investigation, on model-predicted response values.
Let n be the number of design points and p the number of parameters in the model. The model can be written in matrix notation as :

$$\mathbf{Y} = \mathbf{XB} + \mathbf{e} \quad \text{(eq. 3)}$$

where **Y** is the (n×1) vector of responses, **X** the (n×p) matrix of model terms, **B** is the (p×1) vector of unknown coefficients, and **e** is the (n×1) vector of errors with zero means and variance $\sigma^2\mathbf{I}$, σ^2 being the experimental error variance and **I** the (n×n) identity matrix. $\hat{\mathbf{B}}$, the least squares estimate of **B**, is defined by:

$$\hat{\mathbf{B}} = (\mathbf{X}'\mathbf{X})^{-1}\mathbf{X}'\mathbf{Y} \quad \text{(eq. 4)}$$

It can be shown that the variance-covariance matrix for $\hat{\mathbf{B}}$ checks :

$$\mathrm{Var}(\hat{\mathbf{B}}) = (\mathbf{X}'\mathbf{X})^{-1}\sigma^2 \quad \text{(eq. 5)}$$

and, for prediction models, that the prediction variance at point **x** is :

$$\mathrm{Var}(\mathbf{x}) = d_x \sigma^2 \quad \text{(eq. 6)}$$

where $d_x = \mathbf{x}'(\mathbf{X}'\mathbf{X})^{-1}\mathbf{x}$ and **x** is a (1×p) vector.
Equations (5) and (6) are most important since they show how the experimental error affecting the response is transmitted to the estimates of the model coefficients and to the predicted response at point **x**. Two terms must be taken into account: the experimental error, which is not surprising, and matrix **X**, i.e. the distribution of the experimental points within the experimental domain and the analytical form of the model. As σ^2 is imposed by the environment, it is thus on matrix **X** that one should play to improve the model precision. Designs have been optimized for a wide variety of problems.

Performing of the Experiments

The trials must then be performed very carefully according to plan. The experimenter should be aware that errors in experimental procedure at this stage can dramatically affect the relevance of the design strategy.

Statistical analysis of the Data

The model coefficients are estimated by least squares regression techniques (see eq. 4), and possible model deficiencies are looked for by analysis of variance. Provided the variance of the experimental error is estimated using replicated runs, a test for significance of regression can be carried out by assuming that all coefficients β_i are zero. Rejection of this hypothesis implies that at least one of the regressor variables x_i contributes significantly to the model. In the case of response surface investigation, when there are degrees of freedom to calculate the residuals, model adequacy is first checked by verifying that the lack of fit of the model is statistically not significant. Once the data have been analyzed, practical conclusions are drawn from the results. They should be validated by performing confirmation testing.

USE OF DOE FOR FACTOR SCREENING

To investigate the robustness of the cement recipe given in Table II, the first objective was to determine, among all the waste components listed in Table I, those which significantly influenced the properties of the cement-waste forms when they varied within the experimental domain of interest. Experiments were organized according to a screening design.

Experimental Design Construction

The experimental design construction was based on the following procedure [2]:

(i) selection of the variables (or factors) and experimental region of interest given the objectives of the study,
(ii) selection of the responses to characterize the phenomenon under investigation,
(iii) assumption of an empirical model for the responses, and
(iv) selection of a design that provided good estimates of the parameters in the model.

Factors and experimental domain

Table I illustrates the expected variations in the waste composition by means of a high and low value for each of its components. Since electroneutrality of the solution should be satisfied, the sodium concentration was regarded as a dependant parameter for balancing positive and negative charges. This means H^+, Cl^-, F^-, NO_3^-, PO_4^{3-}, SO_4^{2-} Al^{3+}, Ca^{2+}, Fe^{3+}, Ce^{3+}, Pb^{2+}, SiO_2, Zn^{2+}, B and the organics could vary independently in the domain of interest, bringing the total number of independent factors to 15. Given the low concentration of Ce^{3+}, SiO_2, Zn^{2+}, B and the organics, they were grouped in one factor, referred as “minors” (Table I).

Responses

Each elaborated cement-waste form was evaluated for a number of properties including setting time, bleeding, fluidity after mixing, rise in temperature during hydration, compressive strength and dimensional stability. The desirable criteria were defined by taking into account both process requirements and near-surface disposal specifications (Table III). In this paper, the focus was placed on the properties of the waste-form at an early age (Table IV).

TABLE IV. Investigated responses and associated variance of the experimental error (previously determined on replicated runs).

Criteria	N°	Response	Unit	St. dev.	Var.	D.F
Process requirements	1	NaOH required	[ml/2L]	8.41	70.73	3
	2	Dry extract of the sludge	[g/100ml]	0.70	0.49	3
	3	Initial viscosity at t_0	[Pa.s]	0.40	0.16	3
	4	Equilibrium viscosity at t_0	[Pa.s]	0.32	0.10	3
	5	Initial viscosity at t_0+30 min	[Pa.s]	0.45	0.20	3
	6	Equilibrium viscosity at t + 30 min	[Pa.s]	0.21	0.04	3
	7	Beginning of setting	[hour]	2.22	4.93	3
	8	End of setting	[hour]	0.75	0.56	3
Disposal specifications	9	Bleedwater @ 48 h	[%]	0.00	0.00	3
	10	Maximum temperature during hydration	[°C]	1.21	1.46	3
	11	Heat of hydration	[j/g_{cement}]	16.87	284.60	3
	12	Time of maximum temperature	[h]	3.56	12.67	3

Postulated model

Given the high number of factors, a predicting model, which would include higher order terms and interactions, can only be established with a reasonable amount of resources once the main influencing factors have been identified, allowing the others to be neglected. This was the aim of the present work. Therefore, first-order polynomial models were postulated (see Eq. 1) for each response. These models were absolutely not predictive; they only helped exploring many factors in order to reveal whether they had an influence on the responses.

Experimental design

The selected design was a Hadamard matrix, also known as Plackett-Burman (P-B) design [14]. It is an orthogonal two-level experimental design which is very parsimonious since it allows 11 factors to be investigated in 12 runs only. Table V presents the first row of -1 and +1 levels which was used to construct the P-B design. The second row was generated from this first one by moving the elements of the row to the right one position and placing the last element in the first position. A third row was produced from the second similarly, and the process was continued until row 11 was generated. A row of -1 levels was then added, completing the design. The P-B design was at resolution III, meaning that a main effect was partially aliased with every two-factor interaction not involving itself. It was thus useful for efficiently detecting large main effects, assuming all two-factor interactions were negligible in relation to the important main effects.

TABLE V. +1 and -1 levels for the P-B design (12 runs).

+1	+1	-1	+1	+1	+1	-1	-1	-1	+1	-1

EXPERIMENTAL

Preparation of Synthetic Waste and Pre-treatment

Waste surrogates were prepared according to the experimental plan (Table VI) by diluting a 10 mol/L nitric acid solution and by dissolving sodium and nitrate salts of analytical grade in demineralized water at 45°C (113°F). The reactant for waste pre-treatment was a solution of technical sodium hydroxide (30 wt.%). In the pre-treatment process, small aliquots were progressively added to the simulated waste under stirring. The pH of the suspension was measured after an equilibration time of 72 hours using a high alkalinity pH sensor (Mettler Toledo InLab Expert Pro) previously calibrated with appropriate buffers between pH 4 and pH 13. If needed the pH was further adjusted to the aimed value of pH 13.0. The dry residue was measured by oven drying at 105°C (221°F).

Cement-Waste Form Elaboration

The pre-treated waste surrogates were cemented using the previously established reference formulation (Table II). 3-L samples were prepared for each trial and characterized for a number of properties according to standardized procedures.

- Viscosity of the grout just after mixing and 30 minutes later was estimated by measuring the torque on a rotating blade at constant speed (100 rpm) in the paste, the initial and equilibrium values were recorded at both measurement times.
- Bleeding was quantified according to French standard NF P 18-359.
- The heat of hydration was measured using Langavant semi-adiabatic calorimetry following EN 196-9 standard. The maximum temperature reached during the test gave a rough estimate of the temperature that may be reached if the cement-waste form was cast in a 200-L metallic drum.
- The setting time was measured by means of an automatic Vicat apparatus according to EN 196-3.

RESULTS AND DISCUSSION

Table VI summarizes the measured responses. As an example, response 6, "*Equilibrium viscosity at t_0+30 min*" i.e. the viscosity of the cement-waste form kept unagitated for 30 minutes after mixing all constituents, is presented in details.

The model coefficients βi were estimated by least squares regression (see eq. 4) using NEMROD software [15]. In multiple linear regression problems, some tests of hypotheses about the model parameters are helpful in measuring the usefulness of the model. Since the designs were saturated, there were no residual degrees of freedom left to calculate the residuals. Thus, the only tested assumption was about the significance of regression: (H_0) the model has no explanatory effect (*i.e.* the regression coefficients are zero). Hypothesis (H_0) being rejected (Table VII), the model was used to interpret the data.

TABLE VII: Checking for significance of model using ANOVA.

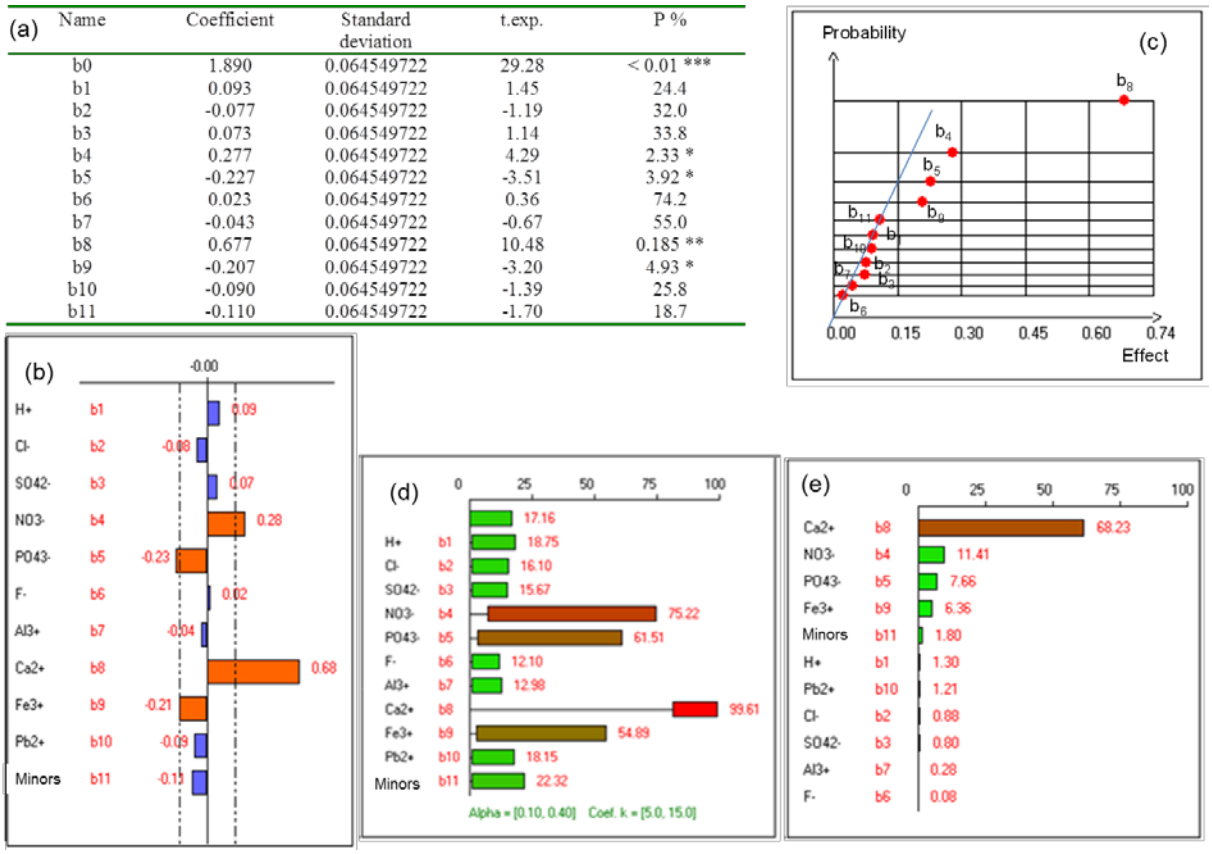
Source of variation	Sum of squares	Degrees of freedom	Mean square	F-test	P-value (%)
Regression	8.0532	11	0.7321	14.6422	2.44 *
Residuals	0.1500	3	0.0500		
Total	8.2032	14			

TABLE VI. Experimental plan and measured responses.

N° Exp	H^+	Cl^-	SO_4^{2-}	NO_3^-	PO_4^{3-}	F^-	Al^{3+}	Ca^{2+}	Fe^{3+}	Pb^{2+}	Ce^{3+}	Zn^{2+}	SiO_2	$B(OH)_3$	Organics
	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	mmol/L	g/L
1	2002.50	22.22	0.00	4815.47	33.17	54.16	250.00	0.00	0.00	8.97	0.00	0.00	0.00	0.00	0.00
2	1308.00	22.22	63.61	3700.00	33.17	54.16	510.00	0.00	0.00	0.00	4.80	10.44	13.64	0.66	0.26
3	2002.50	0.90	63.61	4815.47	0.00	54.16	510.00	106.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4	1308.00	22.22	0.00	4815.47	33.17	0.00	510.00	106.37	99.65	0.00	0.00	0.00	0.00	0.00	0.00
5	1308.00	0.90	63.61	3700.00	33.17	54.16	250.00	106.37	99.65	8.97	0.00	0.00	0.00	0.00	0.00
6	1308.00	0.90	0.00	4815.47	0.00	54.16	510.00	0.00	99.65	8.97	4.80	10.44	13.64	0.66	0.26
7	2002.50	0.90	0.00	3700.00	33.17	0.00	510.00	106.37	0.00	8.97	4.80	10.44	13.64	0.66	0.26
8	2002.50	22.22	0.00	3700.00	0.00	54.16	250.00	106.37	99.65	0.00	4.80	10.44	13.64	0.66	0.26
9	2002.50	22.22	63.61	3700.00	0.00	0.00	510.00	0.00	99.65	8.97	0.00	0.00	0.00	0.00	0.00
10	1308.00	22.22	63.61	4815.47	0.00	0.00	250.00	106.37	0.00	8.97	4.80	10.44	13.64	0.66	0.26
11	2002.50	0.90	63.61	4815.47	33.17	0.00	250.00	0.00	99.64	0.00	4.80	10.44	13.64	0.66	0.26
12	1308.00	0.90	0.00	3700.00	0.00	0.00	250.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

			Viscosity				Bleeding	Vicat setting time		Langavant semi-adiabatic calorimetry		
N° Exp	Volume of NaOH	Dry extract of pre-treated waste	Initial viscosity at t_0	Equilibrium viscosity at t_0	Initial viscosity at t_0 + 30 min	Equilibrium viscosity at t_0 + 30 min	Bleedwater at 48 h	Beginning	End	Maximal temperature	Time of maximal temperature	Heat of hydration
	mL	%	Pa.s	Pa.s	Pa.s	Pa.s	%	h	h	°C	h	J/g
1	587	36.64	1.80	1.00	6.00	1.50	0	9.50	14.00	46.41	45.83	275
2	610	30.51	0.77	0.76	1.10	0.78	1	16.00	31.00	46.30	48.17	251
3	700	45.24	3.60	3.54	3.80	3.70	1	13.00	17.50	50.59	26.17	245
4	639	36.68	2.00	2.05	2.30	2.30	0	15.00	23.00	48.23	26.50	235
5	498	31.60	2.30	2.20	2.70	2.00	1	21.00	28.00	51.75	31.50	244
6	632	39.67	1.35	1.25	1.30	1.20	1.5	18.50	26.50	47.15	41.50	257
7	750	29.64	1.35	1.35	1.60	2.10	1	11.00	18.00	48.15	23.83	227
8	641	28.55	1.87	1.77	2.35	2.30	1	19.00	32.50	49.69	33.83	239
9	813	28.83	0.97	0.93	1.10	1.00	0	8.00	17.00	47.18	30.00	232
10	472	38.26	0.80	0.80	8.00	3.00	0	10.25	14.00	45.93	31.33	237
11	647	40.81	0.60	0.55	3.00	1.30	0	4.00	16.00	45.38	49.00	255
12	461	29.27	0.72	0.70	2.50	1.50	0	2.25	16.50	44.57	30.33	258

Different tools provided valuable information to identify significant effects for each design (Figure 1): calculation of the coefficients significativity (a), coefficient plot showing for i = 1 to 11, the estimate for β_i together with the 95% confidence interval assuming β_i is zero (b), half-normal probability plot of the effects (c), bayesian analysis (d) and Paretto effects (e). The half-normal probability plot, proposed by Daniel [16], is based on the fact that if all estimated effects were noise, they would have a normal distribution and, when plotted on a normal cumulative plot, would fall on a straight line. Hence, effects significantly different from zero should fall outside the normal line. The baysian analysis used here was proposed by Box and Meyer [17]. It involves computing a posterior probability that an effect is active. The prior information is summarized in two parameters, α (the proportion of factors postulated as active) and k (the inflation in the standard deviation produced by an active effect). The calculations were performed for α and k ranging between 0.1-0.4 and 5-15 respectively. The results were presented as a bar graph showing the posterior probabilities. Comparing the Paretto effects, defined for factor X_i as the ratio $b_i^2/\Sigma b_i^2$, is another way to point out the dominating factors influencing the response under study within the experimental domain.



(a)

Name	Coefficient	Standard deviation	t.exp.	P %
b0	1.890	0.064549722	29.28	< 0.01 ***
b1	0.093	0.064549722	1.45	24.4
b2	-0.077	0.064549722	-1.19	32.0
b3	0.073	0.064549722	1.14	33.8
b4	0.277	0.064549722	4.29	2.33 *
b5	-0.227	0.064549722	-3.51	3.92 *
b6	0.023	0.064549722	0.36	74.2
b7	-0.043	0.064549722	-0.67	55.0
b8	0.677	0.064549722	10.48	0.185 **
b9	-0.207	0.064549722	-3.20	4.93 *
b10	-0.090	0.064549722	-1.39	25.8
b11	-0.110	0.064549722	-1.70	18.7

Figure 1: Tools for analyzing response 6 ("Equilibrium viscosity at t_0+30 min").

The conclusions drawn from the different tools were consistent: the most important factor was X_8 (Ca^{2+}). The response was also influenced, but to a lesser extent, by X_4 (NO_3^-), X_5 (PO_4^{3-}) and X_9 (Fe^{3+}). The influence of the other factors could be regarded as negligible within the experimental domain. Increasing the calcium and nitrate concentrations in the waste tended to increase the viscosity of the grout 30 minutes after mixing, whereas the phosphate and iron concentrations had the opposite effect.

The above elaborated approach was applied to all responses (Table VIII). By making a scheme ranking all factors as important (red color in Table VIII), less important (yellow color) and negligible (no color), it appeared the properties at early age of the cement-waste form mainly depended on 5 dominating factors: the molar concentrations of H^+, NO_3^-, F^-, Al^{3+} and Ca^{2+}.

TABLE VIII. Overview of dominating factors for each response.

N°	Response \ Factor	X1	X2	X3	X4	X5	X6	X7	X8	X9	X10	X11
		H^+	Cl^-	SO_4^{2-}	NO_3^-	PO_4^{3-}	F^-	Al^{3+}	Ca^{2+}	Fe^{3+}	Pb^{2+}	Minors
1	Vol. of NaOH required											
2	Dry extract of sludge											
3	Initial viscosity at t_0											
4	Equilibrium viscosity at t_0											
5	Initial viscosity at t_0+30’											
6	Equilibrium viscosity at t_0+30’											
7	Beginning of setting											
8	End of setting											
9	Bleedwater at 48 h											
10	Maximal temperature											
11	Heat of hydration											
12	Time of maximal temperature											

CONCLUSION

In DOE, varying the levels of all factors simultaneously might appear somewhat disturbing at first sight. However, the way in which they are varied is programmed and rational. This method offers many advantages to investigate complex systems such as those encountered in cement-waste formulation. Trials are kept to a minimum, and gradual acquisition of knowledge is possible. In this study, the screening of 16 factors, the components of a concentrated aqueous waste stream, was performed in 12 runs only. Six dominating factors were pointed out: within the experimental domain under investigation, a variation in the molar concentrations of H^+, NO_3^-, F^-, Al^{3+}, Ca^{2+} and Fe^{3+} strongly influenced the properties of the cement-waste form at early age. The next steps will be *(i)* to investigate the possible interactions between these factors and *(ii)* to build operational models from the data which will be used for multi-criteria optimization in order to point out possible waste compositions leading to cement-waste forms of insufficient quality.

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