Application of “Six Sigma™” and “Design of Experiment” for Cementation – Recipe Development for Evaporator Concentrate for NPP Ling AO, Phase II (China) – 12555

Henning Fehrmann, Process Engineer, Westinghouse Electric Germany GmbH

Robert Perdue, Consulting Engineer, Westinghouse Electric Company

ABSTRACT

Cementation of radioactive waste is a common technology. The waste is mixed with cement and water and forms a stable, solid block. The physical properties like compression strength or low leach ability depends strongly on the cement recipe. Due to the fact that this waste cement mixture has to fulfill special requirements, a recipe development is necessary.

The Six Sigma™ DMAIC methodology, together with the Design of experiment (DoE) approach, was employed to optimize the process of a recipe development for cementation at the Ling Ao nuclear power plant (NPP) in China.

The DMAIC offers a structured, systematical and traceable process to derive test parameters. The DoE test plans and statistical analysis is efficient regarding the amount of test runs and the benefit gain by getting a transfer function. A transfer function enables simulation which is useful to optimize the later process and being responsive to changes.

The DoE method was successfully applied for developing a cementation recipe for both evaporator concentrate and resin waste in the plant. The key input parameters were determined, evaluated and the control of these parameters were included into the design.

INTRODUCTION

Westinghouse received a contract for designing a cementation facility for treatment of evaporator concentrates and resins. The system was erected at the Ling Ao site in China. The system consists of an in-drum mixer for 400 l drums. A general overview of the process is shown on Fig. 1. Waste, water and plasticizer are dosed into the drum at a separate filling station. Another powder additive and cement powder is dosed directly into the in-drum mixer during mixing. This makes the system flexible for different waste streams and ensures the optimal recipe for each waste stream. To develop the cementation recipes for evaporator concentrate, the Design of Experiment (DoE) methodology was used. The DoE is an effective way to find the optimal parameters for waste cementation and reduces the risk of failure.

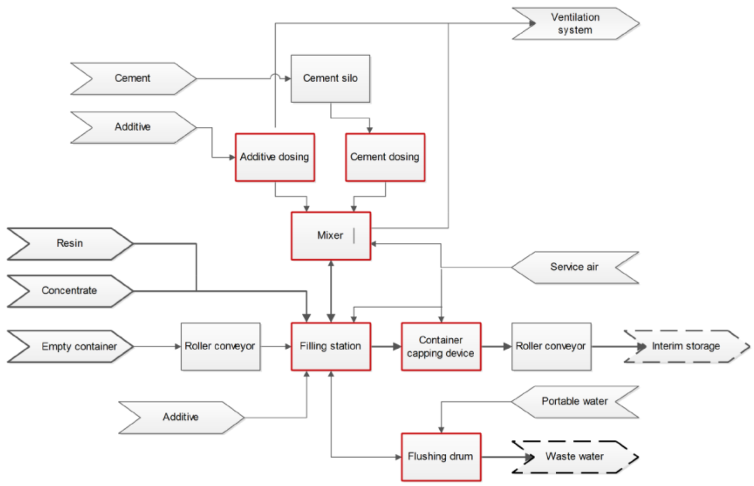


Fig. 1: Cementation process overview

APPLICATION OF "SIX SIGMA™" TOOLS AND "DESIGN OF EXPERIMENT" FOR DEVELOPING A CEMENTATION RECIPE FOR EVAPORATOR CONCENTRATE

For the recipe development, a structured process (basically DMAIC) was used to get from small scale to full scale size. The steps of the DMAIC process are shown in table 1 and will be described in the following paragraphs. The DMAIC process is normally used for the improvement of an existing process. For the recipe development, the DMAIC process was slightly modified to meet the needs for developing a new cementation recipe.

The DoE was applied in the "Analyze" phase for a small scale test.

Table I. Definition von DMAIC

D	**D**efine	Identify the customer and the customer needs and requirements
M	**M**easure	Identify the measuring methods and systems for data collection
A	**A**nalyze	Which Input effects the output?
I	**I**mprove	Determination and optimization of the key input parameters for the best result
C	**C**ontrol	Fixing of the optimum key inputs to ensure the best results possible constantly.

Define phase

The customer's requirement (Voice of the customer) regarding the waste form was captured using the Chinese standard "Characteristic requirement for solidified waste form of low and intermediate level radioactive waste – cement solidified waste form". The process was aided by a tool called a "SIPOC" („**S**uppliers, **I**nputs, **P**rocess, **O**utputs, **C**ustomers"). In general, a standard approach to do a SIPOC is:

1. Definition of system boundaries
2. Capture of the most important process outputs
3. Capture of customer requirements
4. Capture of the most important process inputs

The SIPOC is shown in Fig. 2. The column "Outputs" and "Output Requirements" is the condensed of the "Voice of the Customer" (VOC).
The advantage of the SIPOC is that it provides a well-structured design, summarizing all important information on one page.

Suppliers (Providers of the required resources)	**Inputs** (Resources required by the process)	**Process** (Top level description of the activity)		**Outputs** (Deliverables from the process)	**Customers** (Stakeholders who place the requirements on the outputs)	
		Input Requirements			Output Requirements	
Customer	**evaporater Concentrate**			**Cement block with**		Customer
	- boron content	≤ 40000 ppm		- compression strength	≥ 7 MPa after 28 days	
	- phosphat content	up to 50 g/l		- impact strength from 9m	must stay consistent	
	- sulfate content	up to 20 g/l		- free water	0 % after 7 days	
	- pH-value	neutral = 7		- leaching resistance	Defined leaching rates for ^{60}Co, ^{137}Cs, ^{90}Sr, ^{239}Pu	
				- frost resistance	lost of compression strenghth <25%	
	-total salt content	max. 250 g/l				
				water/cement value	0,3<w/z<0,5	Westinghouse
				resin distribution	homogen	
				water/cement mixture	homogen	
Customer	**Cement quality**					
	- compression strength	minimum 32,5 Mpa				
	- low heat cement	< 220 J/kg				
	- high sulfat resistance					
	- Sodium Equivalent					

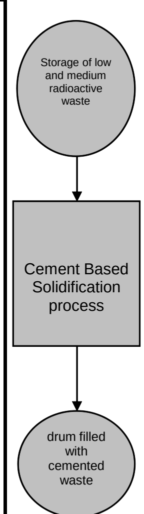


Fig. 2: SIPOC

Measure phase

In this phase the measurement methods and systems are evaluated. Due to the fact that the cementation process was engineered in parallel to the recipe development the key factors have to be determined first before assessing measurement methods and system.

To determine all important inputs and outputs of the cementation process (a more detailed analysis than the SIPOC) different tools were used like e.g. "Fishbone diagram" (see. Fig. 3) or "Cause and Effect matrix" (s. Fig. 4)
The "Fishbone diagram" is a brainstorming tool which catches thoughts, structures and present them in a clear lay out. The head of the fish presents the output factor which is affected by several input variables shown as fish bones.

After identifying all important inputs with the fish bone diagram a “Cause and Effect Matrix (C&E)” was used to prioritize the inputs and to identify the most critical ones. In a C&E Matrix (s. Fig. 4) the “Process Inputs” (or causes) are listed in the left column. The effects (or affected output) are listed in the first three rows (including the importance rating of each parameter). To prioritize each cause and effect combination is evaluated by entering ranking values (like “9” significant impact or “1” for low impact).

The C&E matrix calculates the score for each weighted input parameter. A significant difference in values can normally be seen in this score list (here the score value is 214 to 149). This difference is normally regarded a boundary between significant and less significant input factors.

The inputs with the highest score in the “C&E Matrix” were used as inputs parameters for the Design of Experiment (DoE).

The C&E matrix helps to prioritize and limit the variables to be investigated. But the results have to be judged by the user. For example “Chloride” was not identified by the C&E matrix, but it has a well know effect on cement curing.

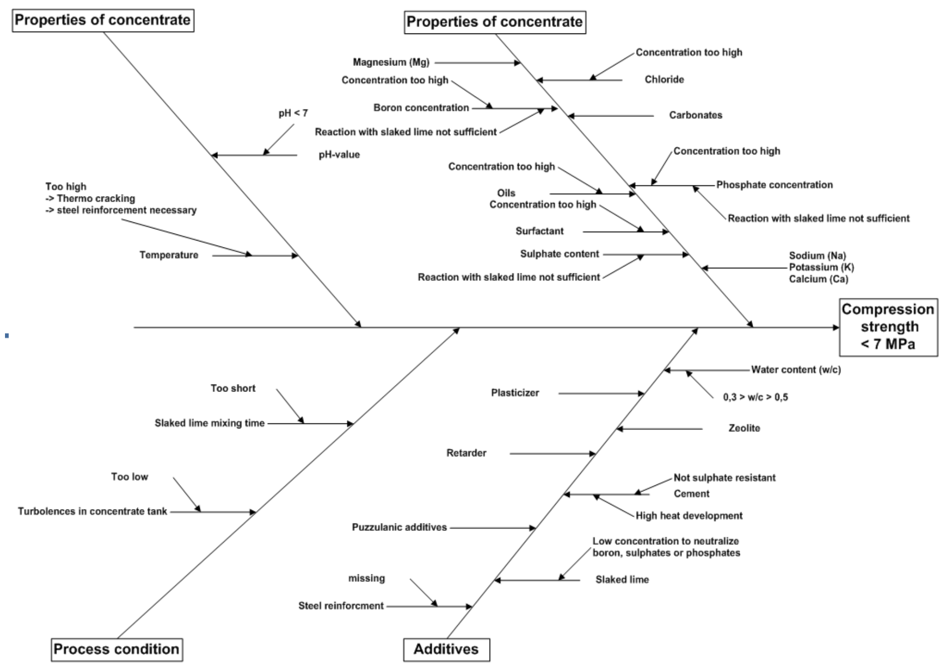


Fig. 3: Fishbone Diagram

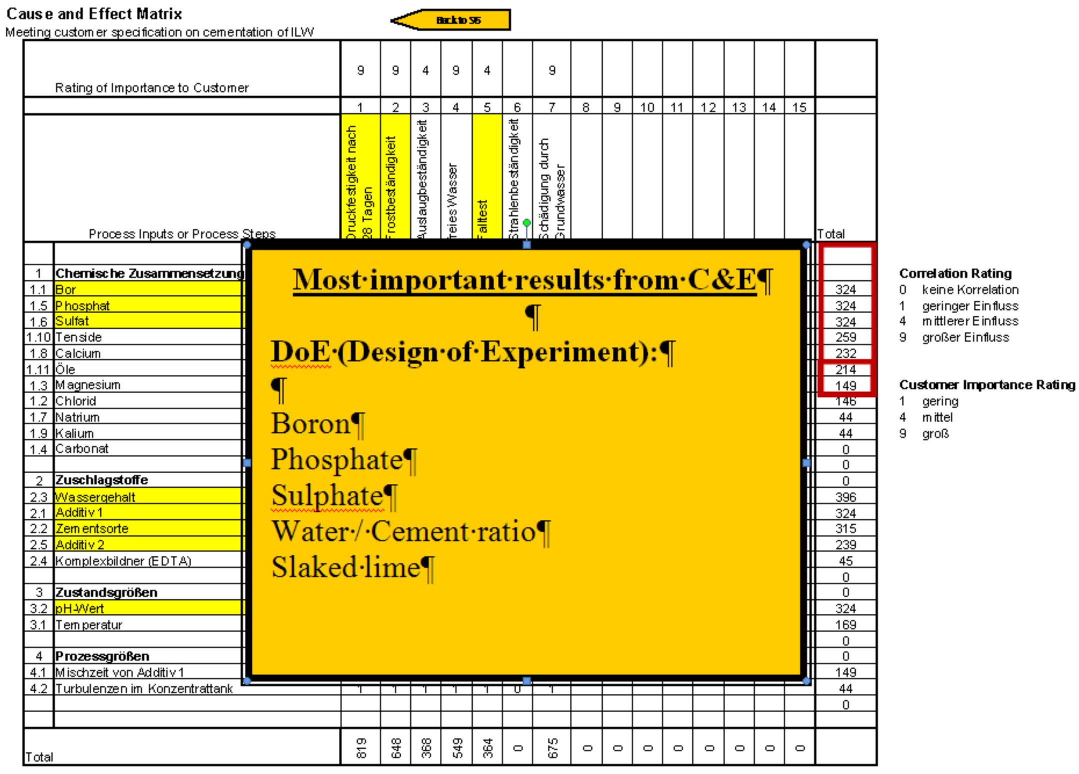


Fig. 4: Cause and Effect Matrix

DESIGN OF EXPERIMENT (DOE) FOR EVAPORATOR CONCENTRATE – ANALYZE PHASE

<u>DoE – definition:</u>

DoE is a method for developing test plans in systematic matter. The test plan is based on statistics. The target of the DoE is to develop a model with all significant inputs (X's) affecting the output (Y). A transfer function is the final result of a DoE which predicts the output. The major advantage of the DoE method is that it is possible to do sensitivity studies and optimization of the process with a relative small number of runs.

Different DoE designs

Different designs for a DoE are available:

- 2-level factorial
- 2-level factorial + centre points
- Responds surface method (Central composite)
- Others

In Fig. 5 different designs are visualized and briefly explained. The test points of a DoE can be regarded as corner points of a cube.

Normally a simple linear approach like “2-level factorial design” is chosen to start (s. Fig. 5). Without centre point non linear behavior is not taken into account therefore it is recommended to add centre points to a “2-level factorial” design when starting tests with an unknown system.

A Responds surface (central composite) design normally is used to gain more detailed knowledge about the system or non linear behavior of the system is already known. For a central composite design the limitation of input factors is very important because it gets larger quickly E.g. 3 input factors:

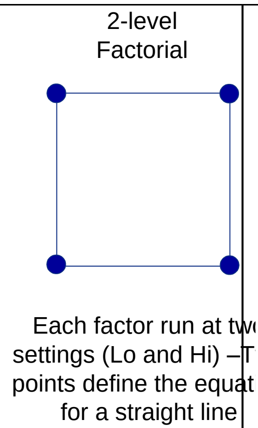
- full factorial design: 2^3 + 1 centre points -> 9 runs
- central composite design: 20 runs (including 6 centre points)

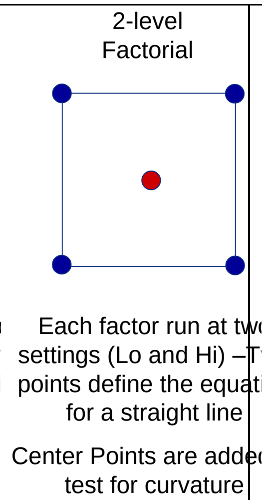
The meanings of the colored dots in Fig. 5 are:

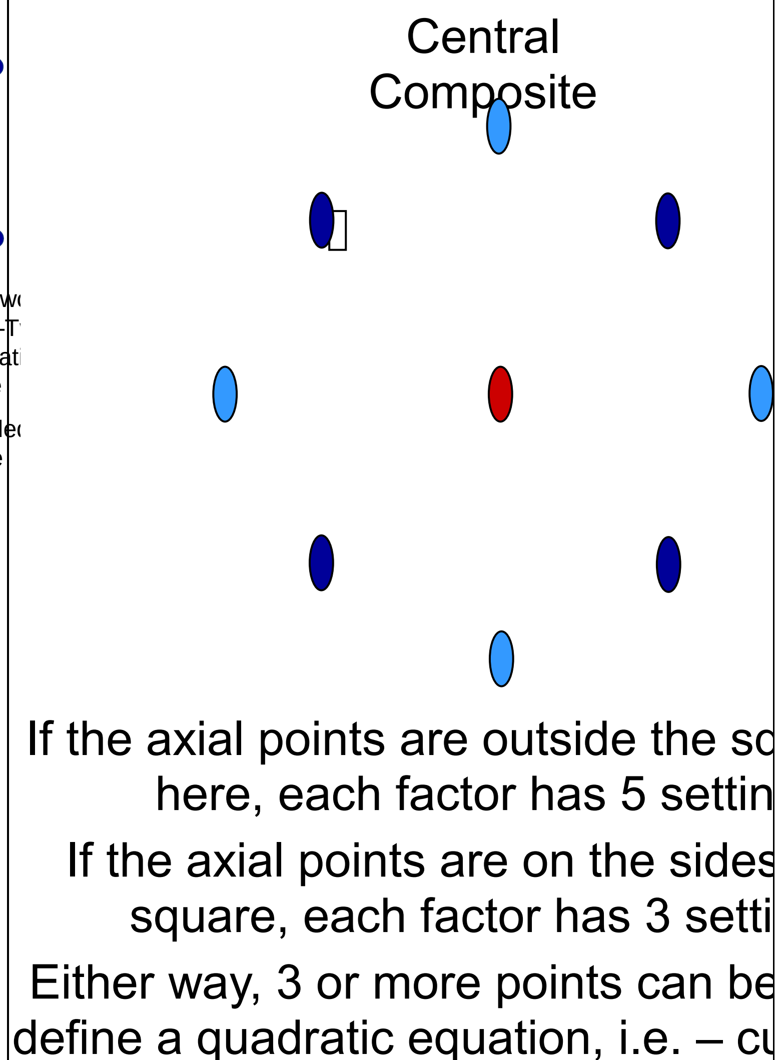
Cube Points

Center Points

Axial points







2 –level factorial design	level factorial design + centre points	central composite design

Fig. 5: different DoE designs

Setting up the DoE for “cementation of evaporator concentrates”

One of the most important steps for a DOE is the limitation of factors to keep the scope as low as possible. With a Cause and Effect Matrix the most important factors influencing the cement performance were determined. An additional factor “Chloride” was included in the DoE due to its known effects on cement curing. In total 6 factors were tested in the DoE.

The DoE was set up as a fractional factorial design with 32 runs + 4 centre points without repetition. In Fig. 6 it is illustrated how to choose a design using the software MINITAB. The green areas indicate a good resolution of the design, whereas yellow or red areas indicate less resolution and therefore less knowledge of the system. This design was chosen to limit the test runs (32 tests instead of 64). The centre points were used to test for curvature in the cement system.

The fractional design offers less detailed information but also less test runs are required. A fractional design is a good choice for an efficient screening.

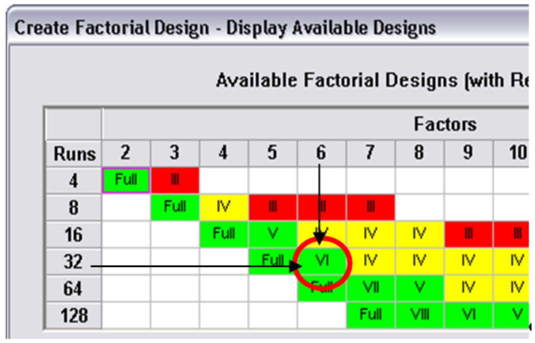


Fig. 6: Choosing DoE design

RESULTS FROM THE DOE “CEMENTATION OF EVAPORATOR CONCENTRATES”

For the data analysis, the MINITAB 15 statistical software was used.

In Fig. 8, Fig. 9 and Fig. 10 excerpt plots from the statistical software are shown. On the left of these plots the input variables are shown. On the right several other calculated values are shown. To build the model to predict the output significant input factors have to be distinguished from insignificant factors. The statistical software helps with that by calculation of so called p-values. If a p-value is < 0,05 this factor has a significant impact on the output. Other values calculated by the statistical software are not discussed in the following.

Also the statistical software can visualize the results to facilitate the data analysis. In Fig. 7 a pareto chart is shown. The horizontal bars represent the input factors and their impact on the modeled compression strength. If a bar is beyond the vertical line this factor has a significant impact.

DoE part 1 (fractional factorial design)

For the selected example “cementation of evaporator concentrates” this results in

- only 2 factors have a significant effect (p-value < 0,05) on the output compression strength (s. Fig. 7 – bar greater than 2,776, Fig. 8 - red marked p-value in the upper part,)
- a non linear impact (curvature) on the prediction of compression strength is significant (s. Fig. 8 - red marks in the lower part)
- further tests have to be done to cover the non linearity and make the model work

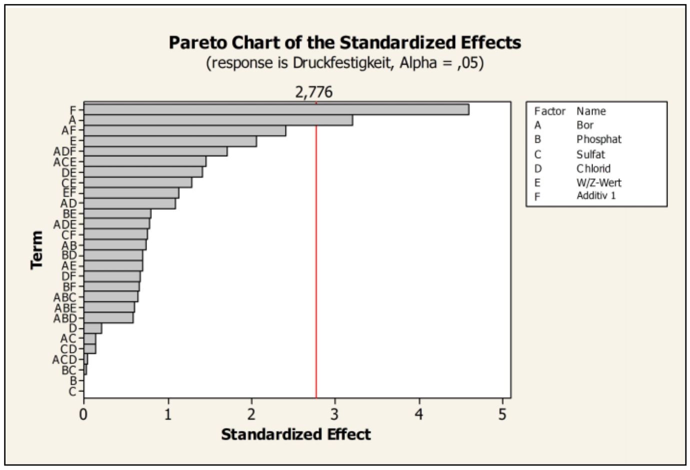


Fig. 7: main effects on compression strength after 28 days

Factorial Fit: Druckfestigk versus Block; Bor [mg/kg]; Phosphat [g/; ...

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* NOTE * This design has some botched runs.  It will be analyzed using a
         regression approach.

Estimated Effects and Coefficients for Druckfestigkeit (coded units)

Term                                  Effect     Coef  SE Coef      T      P
Constant                                        6,272    1,160   5,41  0,006
Block 1                                        -0,712    3,551  -0,20  0,851
Block 2                                         0,585    3,445   0,17  0,874
Block 3                                         0,755    3,551   0,21  0,842
Bor [mg/kg]                           -7,892   -3,946    1,230  -3,21  0,033
Phosphat [g/l]                         0,021    0,010    1,577   0,01  0,995
Sulfat  [g/l]                          0,004    0,002    1,743   0,00  0,999
Chlorid  [g/l]                        -0,501   -0,250    1,230  -0,20  0,849
W/Z-Wert                              -5,059   -2,529    1,230  -2,06  0,109
Calcium-hydroxid                      11,309    5,654    1,230   4,60  0,010
Bor [mg/kg]*Phosphat [g/l]            -2,375   -1,187    1,586  -0,75  0,496
Bor [mg/kg]*Sulfat  [g/l]             -0,331   -0,165    1,230  -0,13  0,900

S = 6,44709   R-Sq = 94,10%   R-Sq(adj) = 48,34%

Analysis of Variance for Druckfestigkeit (coded units)

Source              DF   Seq SS   Adj SS   Adj MS      F      P
Blocks               3    19,07    16,21    5,404   0,13  0,937
Main Effects         6  1700,75  1472,94  245,490   5,91  0,054
2-Way Interactions  15   645,95   669,23   44,615   1,07  0,528
3-Way Interactions   7   283,76   283,76   40,538   0,98  0,543
Residual Error       4   166,26   166,26   41,565
  Curvature          1   160,82   160,82  160,818  88,65  0,003
  Lack of Fit        3     5,44     5,44    1,814
Total               35  2815,80
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Fig. 8: Excerpt from the statistical software (fractional factorial design)

DoE Part 2 (central composite design)

To get the additional test data the statistical software offers the possibility for adding axial points. This is normally the preferred way.

Due to changes in the cement system a new test series had to be conducted because the test data from DoE part 1 are no longer applicable.

In this test series the central composite design was chosen from the beginning to cover for curvature in the model. The factors used were reduced from 6 to 3 factors (instead of 2 as a result from the DoE), because the w/c ratio is known as the important factor for cement (free water, compression strength, leach ability etc.).

The first statistical analysis showed (s. Fig. 9) that interaction effects are not significant in terms of modeling the output results (p – value > 0,05). The target is to reduce the model until only significant terms are left and the R^2(adj) and R^2(pred) is maximized. This is done by simply removing factors from the statistical analysis. In Fig. 10 the statistical analysis of the finally reduced model is shown. Reducing of the model results in finally 5 significant factors (s. Fig. 10) instead of 10 from the first run (s. Fig. 9). Compared to Fig. 9 the R^2(adj) and R^2(pred) is higher and only the significant factors are left. The input w/c stayed in the model because to its known effect on cement compression strength and its p-value very close to 0,05.

Response Surface Regression: MPa versus Boron; w/c; Lime

The analysis was done using coded units.

Estimated Regression Coefficients for MPa

Term	Coef	SE Coef	T	P
Constant	18,1432	2,180	8,322	0,000
Boron	-8,9437	1,366	-6,545	0,000
w/c	-2,6313	1,366	-1,926	0,083
Lime	3,8562	1,366	2,822	0,018
Boron*Boron	-0,8034	1,090	-0,737	0,478
w/c*w/c	0,4591	1,090	0,421	0,683
Lime*Lime	-2,3659	1,090	-2,170	0,055
Boron*w/c	-0,7875	1,932	-0,408	0,692
Boron*Lime	1,6375	1,932	0,847	0,417
w/c*Lime	-2,8125	1,932	-1,455	0,176

S = 5,46593 PRESS = 998,795
R-Sq = 86,35% R-Sq(pred) = 54,36% R-Sq(adj) = 74,06%

Fig. 9: Excerpt from the statistical software (central composite design) first run

Response Surface Regression: MPa versus Boron; w/c; Lime

The analysis was done using coded units.

Estimated Regression Coefficients for MPa

Term	Coef	SE Coef	T	P
Constant	17,819	1,427	12,490	0,000
Boron	-8,944	1,315	-6,800	0,000
w/c	-2,631	1,315	-2,001	0,064
Lime	3,856	1,315	2,932	0,010
Lime*Lime	-2,305	1,009	-2,285	0,037

S = 5,26110 PRESS = 681,891
R-Sq = 81,03% R-Sq(pred) = 68,84% R-Sq(adj) = 75,97%

Fig. 10: Excerpt from the statistical software (central composite design) last run

The result of the response surface design is a transfer function like:

$$Compression\_strength = a_1 \cdot Boron + a_2 \cdot w/c + a_3 \cdot Lime + a_4 \cdot Lime^2 + const. \qquad \text{Eq. 1}$$

Choose optimum settings form DoE results – improve phase

With the transfer function and the statistical data it is possible to predict the compression strength and a confidence interval. The statistical software helps to visualize the results. In s. Fig. 11 a surface plot of the predicted results is shown. The parameters like boron, w/c or lime are given in coded units which mean for example: boron = 1 = 40000 ppm.

The different colors represent areas of predicted compression strength. With that information the optimal settings could be chosen easily. From the identify phase the requirements of compression strength are clear (at least 7 MPa). This means the target for the optimum setting is the light green area (10-20 MPa) shown on the graphs on Fig. 11.
But the optimum settings should be chosen with sufficient margin to cover plant tolerances on the one hand and model uncertainties on the other hand. Scale up effects are not covered in the results a this DoE.

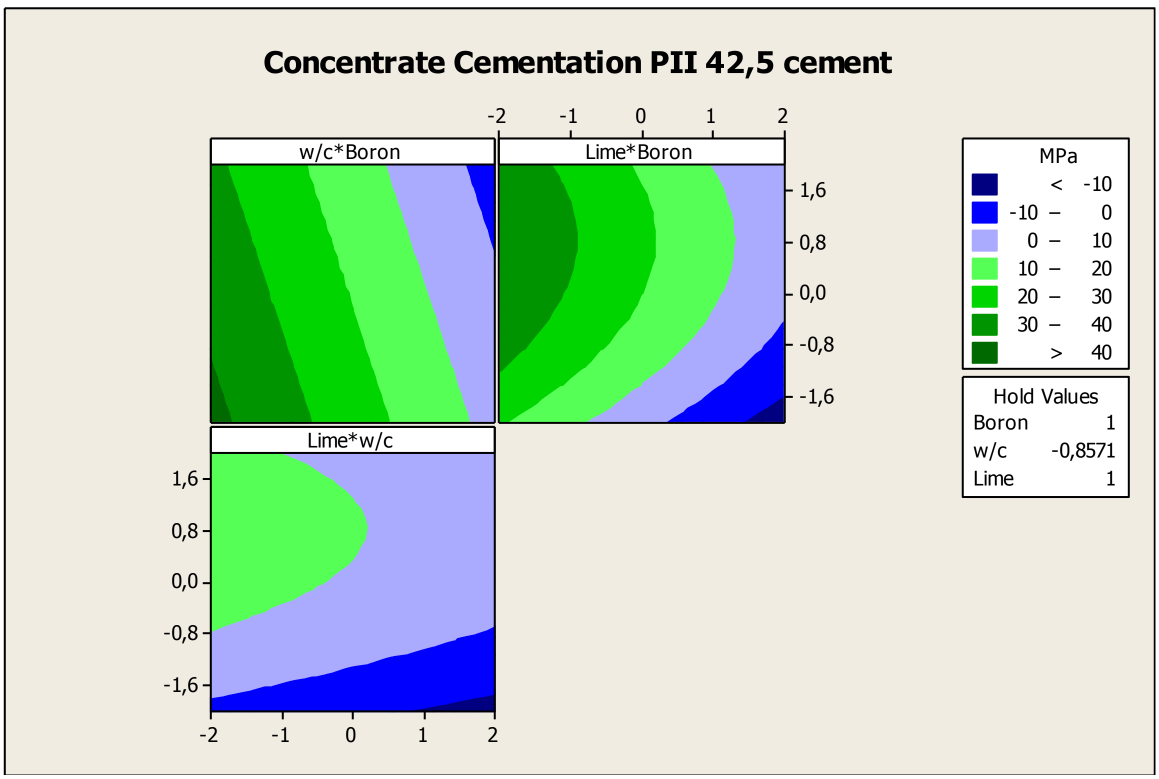

Fig. 11: Contour plot of compression strength for evaporator concentrate cementation

Implement control for key inputs – control phase

The major key input parameters were tested in the DoE. For the full scale plant it was important to control these parameters as well as possible to get reproducible results. This means a volumetric dosing of cement should not be used to eliminate uncertainties coming from variation in bulk density. To control all major key input parameters the dosing of the cementation facility LingAo was designed as a gravimetric dosing (cement, lime, concentrate).

Due to the fact that the lime concentration is linked to the boron concentration the boron content has to be analyzed by taking a small sample. Also the total salinity and density of the concentrate are analyzed.

With the analyzed concentrate data the PLC program calculates the lime, cement, concentrate and plasticizer mass to be dosed. With that it is ensured that even when having varying concentrate properties the w/c ratio and lime concentration are at the optimum setting.

DISCUSSION

The applied Six Sigma™ tools can help to organize the thinking during the engineering process. Data are organized and clearly presented. Various variables can be limited to the most important ones. The Six Sigma™ tools help to make the thinking and decision process trace able. The tools can help to make data driven decisions (e.g. C&E Matrix). But the tools are not the only golden way. Results from scoring tools like the C&E Matrix need close review before using them.

The DoE is an effective tool for generating test plans. DoE can be used with a small number of tests runs, but gives a valuable result from an engineering perspective in terms of a transfer function. The DoE prediction results, however, are only valid in the tested area. So a careful selection of input parameter and their limits for setting up a DoE is very important. An extrapolation of results is not recommended because the results are not reliable out of the tested area.

REFERENCES

- Six Sigma is a federally registered trademark of Motorola, Inc.
- MINITAB is a federally registered trademark of Minitab, Inc.