ONDRAF/NIRAS

DoE in the field of nuclear waste management.

Some case studies

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What is DoE

A statistical tool allowing to gain maximum information out of a minimum of experimental trials.

- Especially useful if e.g. only limited experiments can be conducted, due to time, money, risks, … .

Also, from a project mgmt. point of view:

- helps to structure research projects;
- stay focus on the end goal;
- aid in decision making.

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Case study: Pu sorption

Context and introduction

Case study: Pu sorption

Context and introduction

Since the mobility (leaching) of radionuclides through engineered barriers is greatly affected by the sorption properties, knowledge on these properties is of uttermost important in the frame work of the safe disposal of radioactive waste.

Photo of a pilled up nuclear waste at a temporary storage site.

Case study: Pu sorption

Context and introduction

Pu – plutonium, with a long half-life and a trace-component of radioactive waste.

Engineered barriers, mainly concrete and mortar, prevent a to fast migration towards the environment.

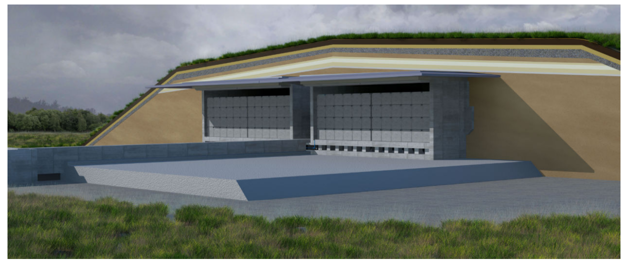

Illustration of a surface repository. The radioactive waste is surrounded by many concrete components, the engineerd barriers.

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Case study: Pu sorption

Context and introduction

A key property affecting the mobility of Plutonium (Pu) through engineered barriers is the sorption parameter, Rd (l/kg).

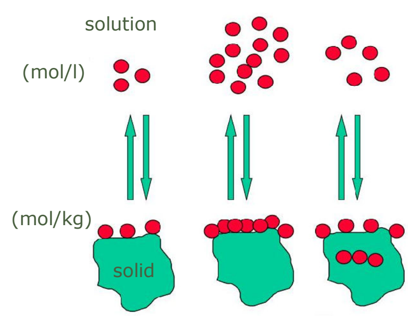

Illustration of sorption of red particles in a solution on a solid phase.

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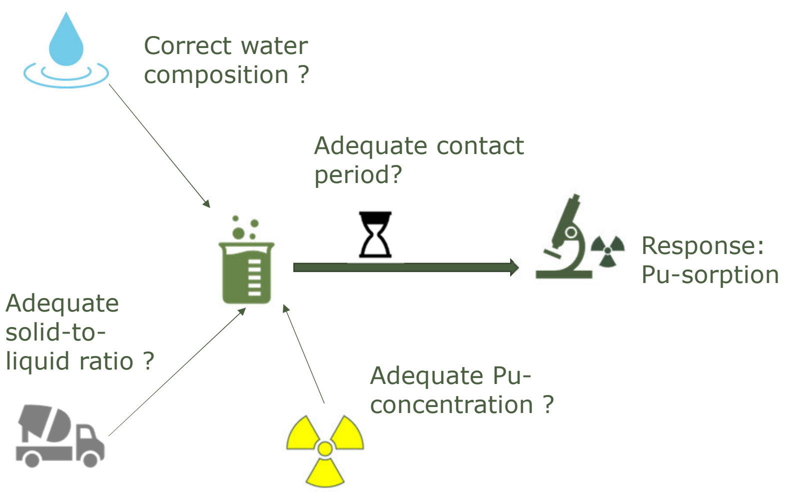
Case study: Pu sorption

Experimental set-up



Case study: Pu sorption

Screening design

A structured research

1. Uncertainties were listed and bounded (high vs low)
2. We discriminated between factors that for sure affect the outcome, and those for which we don't know.
3. A screening study was set-up with:
   - 11 experiments, 9 variables
   - adequate power (80%) to detect effect sizes of 3 Cohen's d at the 5% sign. threshold

Case study: Pu sorption

Screening design

Potential influencing factor

Name	Units	Low	High	Does it affect the outcome
[Cl]	log M	-1.7	0.1	Unsure
$[S^{2-}]$	log M	-4	-1.82	Unsure
[Ca]	log M	-3.3	-2.3	Unsure
pH	-	12.5	13.2	Unsure
Equil. Tijd	days	7	21	Unsure
$[SO_4]$	log M	-4	-1.82	Unsure
Pu	log M	-11	9	Unsure
K	log M	-1.46	-1.30	Unsure
S/L	log g/l	-1	-0.3	Unsure
ISA	log M	-5	-1	**Yes, for sure**

Screening result: ANOVA

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	3.72	7	0.5317	12.42	0.0315
Cl	0.1294	1	0.1294	3.02	0.1805
S^{2-}	0.2783	1	0.2783	6.50	0.0840
Ca	2.88	1	2.88	67.13	**0.0038**
pH	0.0401	1	0.0401	0.9372	0.4044
Equil. Tijd	0.1639	1	0.1639	3.83	0.1454
SO_4	0.0615	1	0.0615	1.43	0.3170
Pu, S/L, K	0.1737	1	0.1737	4.06	0.1375
Residual	0.1285	3	0.0428		
Pure Error	0.0179	2	0.0089		

S/L is the ratio of solid mass to liquid volume in the test tube.
ISA is a degradtion product of cellose, often encoutered in nuclear waste. It is know for reducing sorption.

Clear, and agreed upon, decision rules

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Case study: Pu sorption

Investigations into Ca and ISA

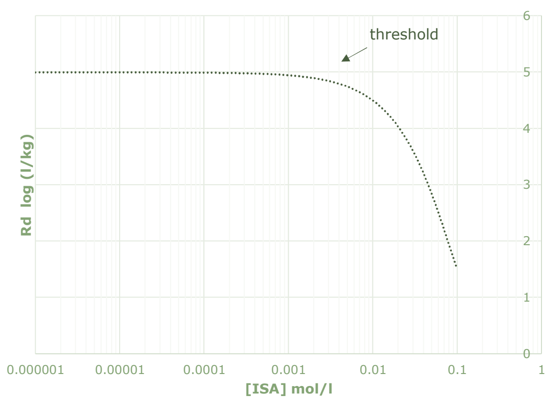

Illustration of how we'd expect Rd to evolve in function of [ISA]. Based on literature on similar materials

Research question (RQ) 1:

What is Rd in function of ISA (and Ca) ?

Research question 2:

Where is the threshold ?

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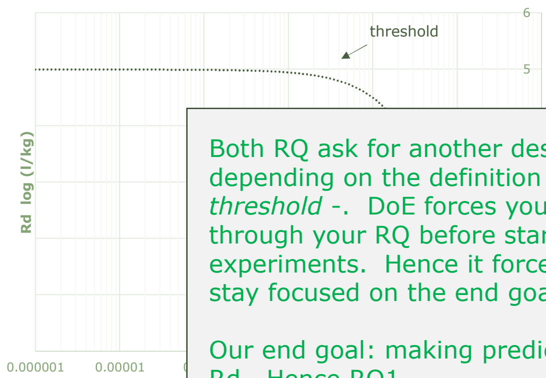
Case study: Pu sorption

Investigations into Ca and ISA



Both RQ ask for another design – depending on the definition of *threshold* -. DoE forces you to think through your RQ before starting the experiments. Hence it forces to stay focused on the end goal.

Our end goal: making predictions of Rd. Hence RQ1.

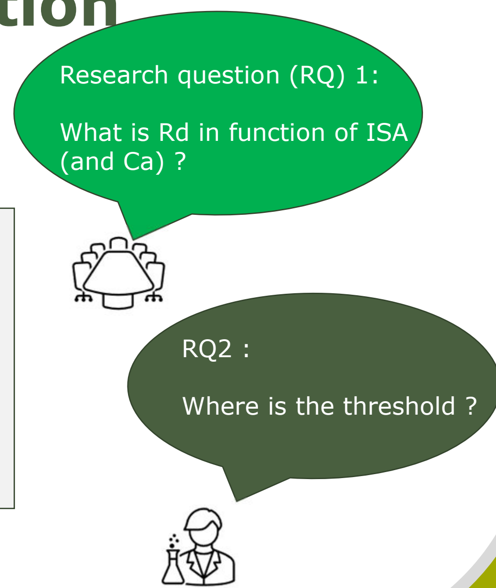
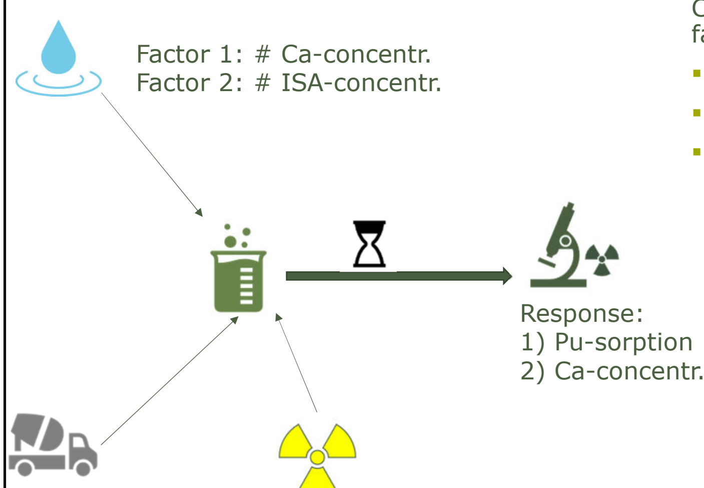


Illustration of how we'd expect Rd to evolve in function of [ISA]. Based on literature on similar materials

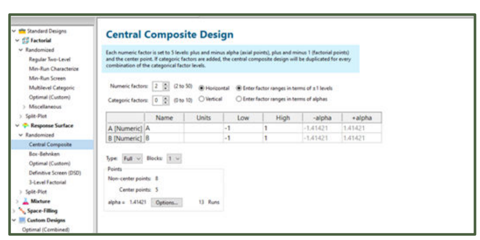
Case study: Pu sorption

Experimental set-up and design



Central Composite Design (CCD): in two factors

- Complemented with four validation points;
- 17 experiments;
- In most software's library, including SE360 or DX.



Case study: Pu sorption

Experimental set-up and design – Analysis and interpr.

ANOVA						
Source	**Sum of Squares**	**df**	**Mean Square**	**F-value**	**p-value**	
Model	4.60	5	0.9196	219.58	< 0.0001	significant
A-[Ca^{2+}]	0.1713	1	0.1713	40.90	0.0007	
B-[ISA]	2.37	1	2.37	565.26	< 0.0001	
AB	0.0647	1	0.0647	15.44	0.0077	
A^2	0.0282	1	0.0282	6.73	0.0410	
B^2	1.27	1	1.27	304.12	< 0.0001	
Residual	0.0251	6	0.0042			
Lack of Fit	0.0019	2	0.0009	0.1619	**0.8558**	**not significant**
Pure Error	0.0232	4	0.0058			
Cor Total	4.62	11				

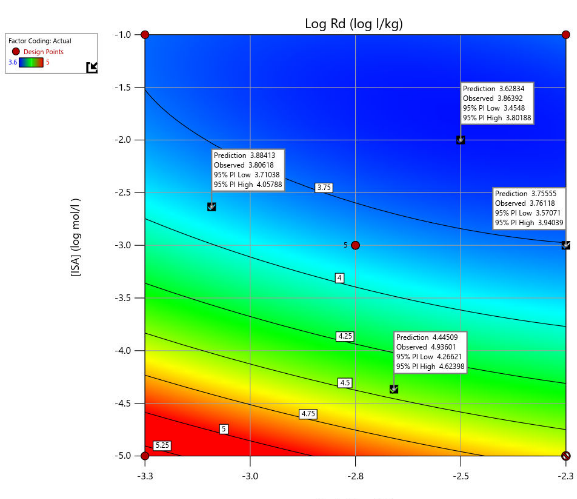
Fit statistics			
Std. Dev.	0.0647	**R^2**	0.9946
Mean	4.13	**Adjusted R^2**	0.9900
C.V. %	1.57	**Predicted R^2**	0.9861

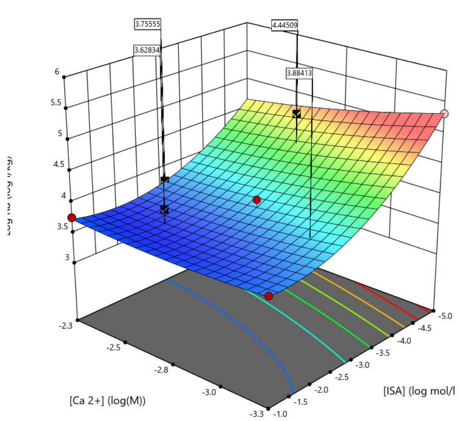
Validation points			
Actual Value	**Predicted Value**	**-95% PI**	**+95% PI**
3.864	3.628	3.45	3.80
3.806	3.884	3.71	4.06
4.936	4.445	4.27	4.62
3.761	3.756	3.57	3.94

The model is probably close to reality but might be an underestimation at low ISA-concentr. (high Rd-values)

Case study: Pu sorption

Experimental set-up and design – Analysis and interpr

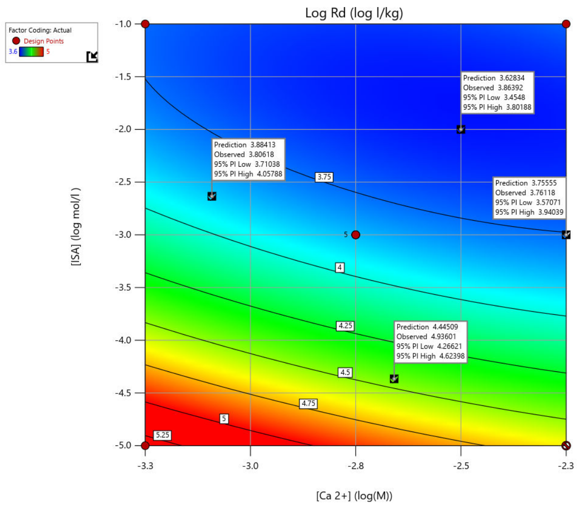


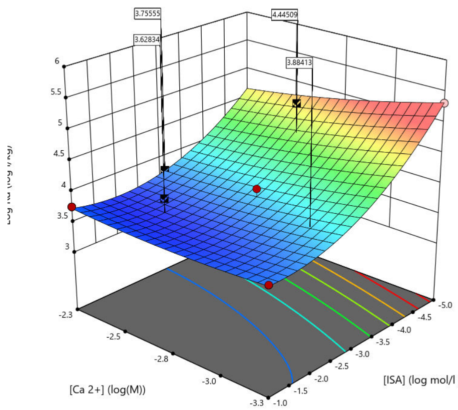


Case study: Pu sorption

Experimental set-up and design – Analysis and i

" Now tell me, what is Rd in function of ISA only ? "





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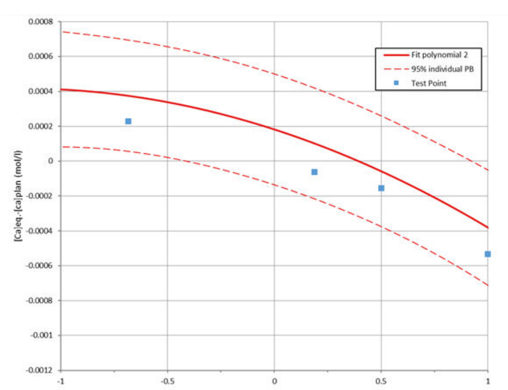
Case study: Pu sorption

Intrinsic calcium-concentration

" Now tell me, what is Rd in function of ISA? "

An additional response was defined : $[Ca^{2+}]_{eq.} - [Ca^{2+}]_{plan}$.



This model was used to estimate the confidence region of $[Ca]_{plan}$ for which $[Ca^{2+}]_{eq.} - [Ca^{2+}]_{plan} = 0$.

Since there is uncertainty on the model coefficients, it is not the intercept of this model with y=0.

We applied the approach published by Box and Hunter in 1954 [i]. Taking into account the variance and covariance of the model coefficients.

Which resulted in, for 95% conf., [0.174; 0.586] coded or [1.95; 3.09] mM actual Ca-concentr.

[i]: G.E.P. Box and J.S. Hunter, *A confidence region for the solution of a set of simultaneous equations with an application to experimental design,* Institute of statistics Mimeo series No. 72, June, 1953.

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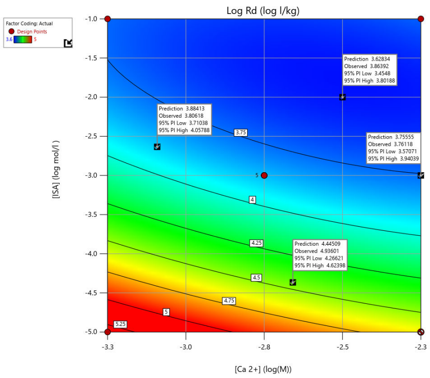
Case study: Pu sorption

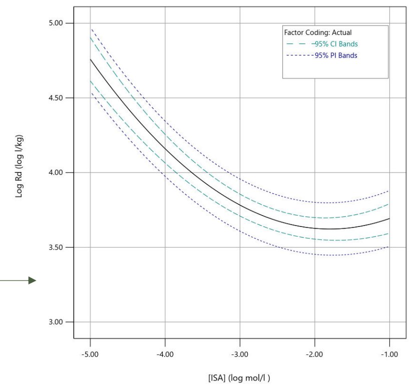
Pu-sorption in function of ISA at the intrinsic Ca-c

" Now tell me, what is Rd in function of ISA? "



In the region [$10^{-2.7}$; $10^{-2.5}$] mM Ca, the higher boundary gives the lowest Rd-values of the two.

Hence, one can calculate the model for a fixed Ca-concentration at $10^{-2.5}$ M



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Case study: Pu sorption: the sequel

Context and introduction

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Case study: Pu sorption: the sequel

Context and introduction

" What if the lower boundary of Cl is lower as anticipated ?"

Photo of a pilled up nuclear waste at a temporary storage site.

Case study: Pu sorption: the sequel

Context and introduction

" What if the lower boundary of Cl is lower as anticipated ?"

Let's vary chloride between:
Absolute null and 1.25 mol/l

H_0: $\mu_a - \mu_b = 0$
H_a: $\mu_a - \mu_b \neq 0$

$P < 0.0001$

H0 is – unfortunately - rejected

Case study: Pu sorption: the sequel

An augment

What now?

Let's augment the model for different Chloride conc.

This would ask for at least 5 experiments:

- 1 block-effect;
- 1 quadratic effect;
- 1 linear effect;
- 2 interactions.

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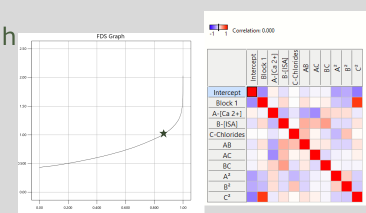
Internal slide

u sorption

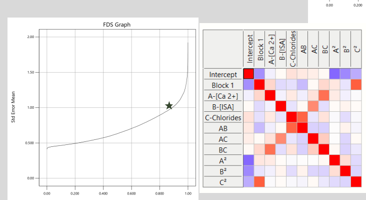
From current design to **augment**

5 + 1 model experiments

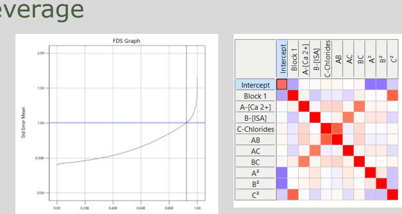
4 exp. with high leverage



5 + 2 model experiments



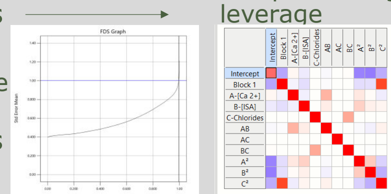
4 exp. with high leverage



5 + 3 model experiments

4 exp. with high leverage

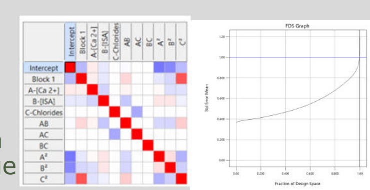
no exp. with high leverage



5 + 4 model experiments

5 + 5 model experiments

no exp. with high leverage



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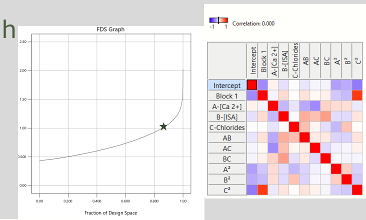
Internal slide

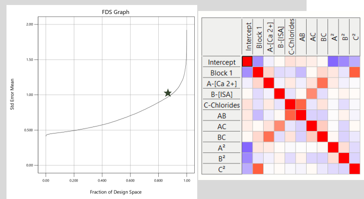
u sorption

From current design to **augment**

4 exp. with high leverage

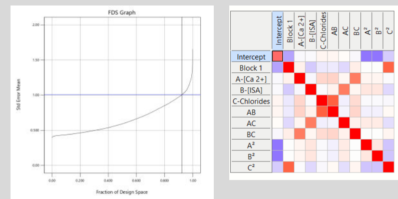


5 + 1 model experiments



4 exp. with high leverage

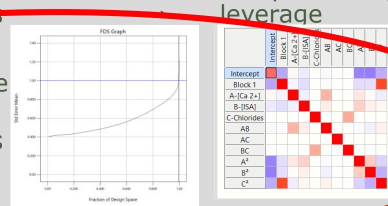
5 + 2 model experiments



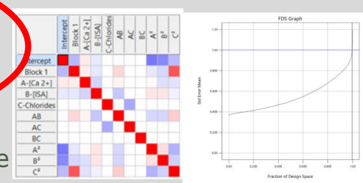
4 exp. with high leverage

5 + 3 model experiments

no exp. with high leverage



5 + 4 model experiments



5 + 5 model experiments

no exp. with high leverage

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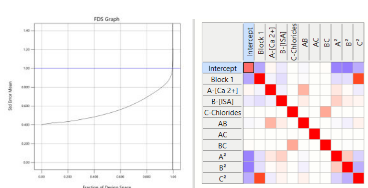
Case study: Pu sorption: the sequel

An augment

5 + 4 model experiments

no exp. with high leverage



To capture (changes of) exp. error 6 repeated center runs were added.

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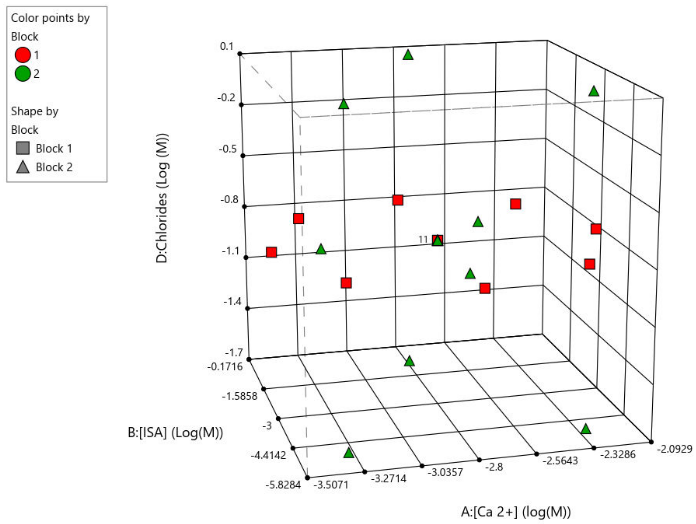
Case study: Pu sorption: the sequel

An augement



Case study: Pu sorption: the sequel

An augement + additional verification runs

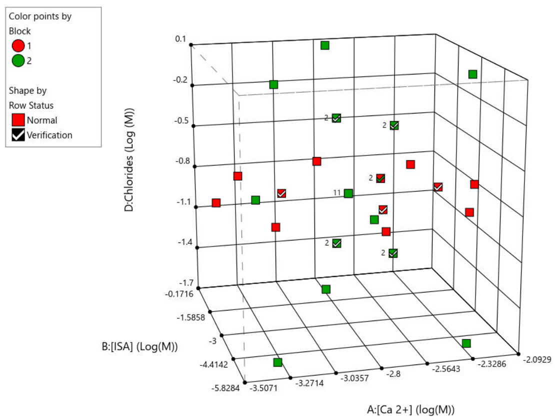
Additional verification runs were added at four treatments.

These verification runs were decided to be executed in two distinct manners:

1. with all other factors at a arbitrary chosen factor level
2. with all other factors at center

Case study: Pu sorption: the sequel

An augement + additional verification runs



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These verification runs were decided to be executed in two distinct manners:

1. with all other factors at a arbitrary chosen factor level
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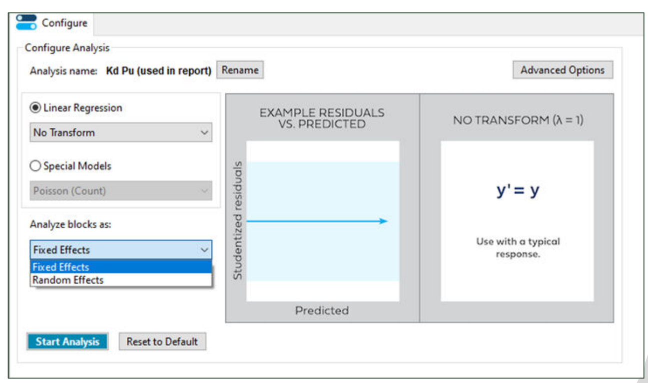
Case study: Pu sorption: the sequel

Analysis - OLS

The analysis of the experimental design was done through OLS (fixed block effects).

It was chosen to do so in lieu of GLS (random block effects) since:

- only two blocks do not allow for assessing the block variance with high precision and;
- lack-of-fit test is (much) easier for fixed block effects.



Case study: Pu sorption: the sequel

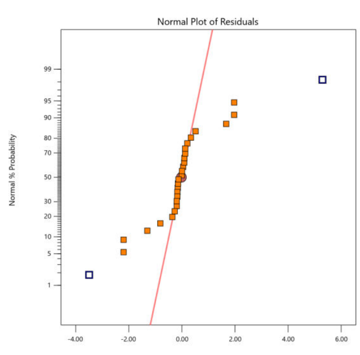
Analysis – ANOVA (all data, a priori model)

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Block	0.0696	1	0.0696			
Model	30.92	9	3.44	8.96	< 0.0001	significant
A-[Ca^{2+}]	0.0128	1	0.0128	0.0335	0.8569	
C-[ISA]$_{corrected}$	5.78	1	5.78	15.07	0.0012	
D-Chlorides	0.0892	1	0.0892	0.2327	0.6357	
AC	0.1535	1	0.1535	0.4005	0.5352	
AD	1.59	1	1.59	4.15	0.0574	
CD	0.2373	1	0.2373	0.6190	0.4422	
A²	0.5336	1	0.5336	1.39	0.2543	
C²	4.30	1	4.30	11.23	0.0038	
D²	0.0010	1	0.0010	0.0025	0.9604	
Residual	6.52	17	0.3833			
Lack of Fit	6.48	8	0.8098	196.67	< 0.0001	significant
Pure Error	0.0371	9	0.0041			
Cor Total	37.50	27				

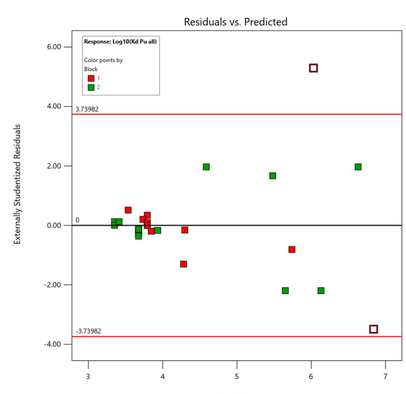
Higher order terms are at play and/or some experiments are erroneous

Case study: Pu sorption: the sequel

Analysis - residuals



- Residuals are clearly not N-distributed.
- Run 11 and Run 6 are the extreme deviating residuals.
- Run 11 and Run 6 are the runs with the highest Rd-values in block 1
- Rd-measurements are often difficult for experiments with high Rd-value (i.e., low ISA).



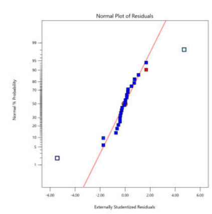
Case study: Pu sorption: the sequel

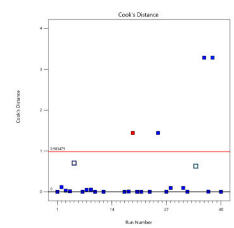
Analysis – data minus 11 and 6, a priori model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Block	0.6194	1	0.6194			
Model	21.82	9	2.42	27.41	< 0.0001	significant
A-[Ca^{2+}]	0.0885	1	0.0885	1.00	0.3331	
C-[ISA]$_{corrected}$	5.06	1	5.06	57.23	< 0.0001	
D-Chlorides	0.0892	1	0.0892	1.01	0.3312	
AC	0.0176	1	0.0176	0.1986	0.6622	
AD	1.59	1	1.59	18.01	0.0007	
CD	0.2373	1	0.2373	2.68	0.1222	
A^2	0.0311	1	0.0311	0.3513	0.5622	
C^2	3.94	1	3.94	44.60	< 0.0001	
D^2	0.0000	1	0.0000	0.0001	0.9914	
Residual	1.33	15	0.0884			
Lack of Fit	1.29	6	0.2149	52.19	< 0.0001	significant
Pure Error	0.0371	9	0.0041			
Cor Total	23.76	25				

← Model.
- Lack-of-fit
- Might be simplified

↓ Run 5 and Run 34.
- Deviating residuals;
- Small D-cook (e.i. small effect on model);
- Relative high Rd





Still a lack of fit

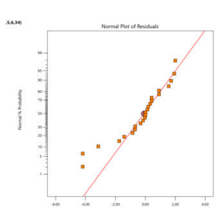
Case study: Pu sorption: the sequel

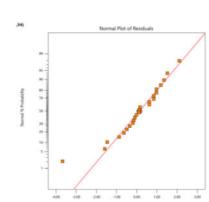
Analysis – data minus 11, 6, **5 and 34**, a priori model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Block	0.5271	1	0.5271			
Model	16.71	9	1.86	241.10	< 0.0001	significant
A-[Ca 2+]	0.1321	1	0.1321	17.16	0.0012	
C-[ISA]corrected	4.36	1	4.36	566.02	< 0.0001	
D-Chlorides	0.0892	1	0.0892	11.59	0.0047	
AC	0.1536	1	0.1536	19.95	0.0006	
AD	1.59	1	1.59	206.83	< 0.0001	
CD	0.2373	1	0.2373	30.82	< 0.0001	
A^2	0.0796	1	0.0796	10.34	0.0068	
C^2	1.90	1	1.90	246.35	< 0.0001	
D^2	0.0160	1	0.0160	2.07	0.1735	
Residual	0.1001	13	0.0077			
Lack of Fit	0.0630	4	0.0158	3.83	0.0439	significant
Pure Error	0.0371	9	0.0041			
Cor Total	17.33	23				

← Model.
- Lack of fit
- Model can be simplified

↓ Residuals.
- No clear small set of deviating residuals
- Unless simplified model is used
  - Run 9, small D-cook





Still a lack of fit, but better

Case study: Pu sorption: the sequel

Analysis – # data sets, hence # models and # residuals

	Log_{10}(Kd Pu) all	Log_{10}(Kd Pu) minus 11	Log_{10}(Kd Pu) minus 11, 6	Log_{10}(Kd Pu) minus 11, 6,5	Log_{10}(Kd Pu) minus 11,6,5,34	Log_{10}(Log Kd Pu) minus 11, ,6,5,34,9
	3.54	3.52	3.54	3.52	3.52	3.52
A [Ca^{2+}]	**-0.0381**	**-0.0522**	**-0.1004**	-0.1233	-0.123	-0.1275
C [ISA_{corr^-}]	-0.9209	-1.02	-0.8926	-0.9925	-0.9093	-0.8631
D [Cl^-]	-0.1396	-0.1396	-0.1396	-0.1396	-0.1396	-0.1396
AC	**-0.1791**	**-0.1833**	**0.0642**	**0.1962**	0.1976	0.1948
AD	0.6309	0.6309	0.6309	0.6309	0.6309	0.6309
CD	0.2515	0.2515	0.2515	0.2515	0.2515	0.2515
A^2	**0.2485**	**0.0728**	0.0628	0.0577	0.1029	0.0727
C^2	1.06	1.59	1.26	1.51	1.2	1.45
D^2	0.0201	-0.2697	-0.0022	-0.185	0.1118	-0.054
Lack-of-fit	<0.01%	<0.01%	<0.01%	**0.2%**	**4.39%**	**29,44%**
st. dev.	NA	NA	NA	NA	NA	0.0676

Effect on model coeif. → Effect on est. exp. error distr. →

Case study: Pu sorption: the sequel

Analysis – # data sets, hence # models and # residuals

	Log_{10}(Kd Pu) all	Log_{10}(Kd Pu) minus 11	Log_{10}(Kd Pu) minus 11, 6	Log_{10}(Kd Pu) minus 11, 6,5	Log_{10}(Kd Pu) minus 11,6,5,34	Log_{10}(Log Kd Pu) minus 11, ,6,5,34,9
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Lack-of-fit	<0.01%	<0.01%	<0.01%	0.2%	4.39%	29,44%
st. dev.	NA	NA	NA	NA	NA	0.0676

Effect on model coeif. → Effect on est. exp. error distr. →

- Model is stable after deselecting Run 11, 6 and 5.
- Deselecting additionally Run 9 and 34 changes estimate for the exp. error (0.0676 log l/kg), but not the model.

It was opted to:

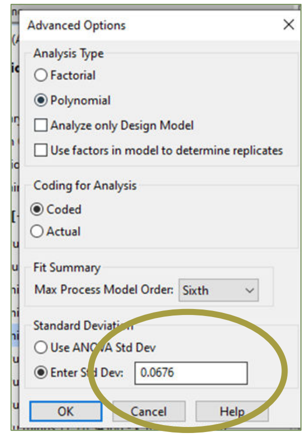
1. Deselect Run 11, 6 and 5
2. Force the standard deviation of the exp. error to 0.0676
3. Fit through OLS and simplify model

Case study: Pu sorption: the sequel

Analysis – data minus 11, 6, 5 - forced st. dev

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Block	1.19	1	1.19			
Model	20.69	7	2.96	93.56	< 0.0001	significant
A-[Ca^{2+}]	0.1440	1	0.1440	4.56	0.0486	
C-[ISA]$_{corrected}$	6.52	1	6.52	206.37	< 0.0001	
D-Chlorides	0.0892	1	0.0892	2.82	0.1124	
AC	0.1519	1	0.1519	4.81	0.0435	
AD	1.59	1	1.59	50.39	< 0.0001	
CD	0.2373	1	0.2373	7.51	0.0145	
C^2	7.23	1	7.23	228.93	< 0.0001	
Residual	0.5056	16	0.0316			
Lack of Fit	0.4685	7	0.0669	16.25	0.0002	significant
Pure Error	0.0371	9	0.0041			
Cor Total	22.39	24				

Anticipated lack of fit



Category 1 - BEDRIJFSVERTROUWELIJK_CONFIDENTIEL D'AFFAIRES

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Case study: Pu sorption: the sequel

Analysis – data minus 11, 6, 5 - forced st. dev

Verification runs are well predicted by the model. Differences are small in relative values and mostly well within the PI's.

Conclusion: this model is applicable, very probable close to reality

Run	Predicted	Observed	-95% PI	+95 % PI	(Obs – Pred) / Obs	Fit?
Run 13	3.341	**3.864**	**3.190**	**3.492**	**+13%**	☹
Run 14	3.661	3.806	3.509	3.812	+4%	☺☺
Run 15	5.063	4.936	4.912	5.214	-3%	☺☺
Run 16	3.608	3.761	3.453	3.763	+4%	☺☺
Run 22 *	3.337	3.351	3.184	3.491	+4%	☺☺
Run 24 *	3.728	3.652	3.574	3.883	-2%	☺☺
Run 26	3.593	**3.435**	**3.439**	**3.747**	-5%	😐
Run 29 *	3.593	**3.428**	**3.439**	**3.747**	-5%	😐
Run 30	3.728	**3.484**	**3.574**	**3.883**	**-7%**	☹
Run 33	3.337	3.378	3.184	3.491	+1%	☺☺
Run 35	3.412	3.356	3.259	3.565	-2%	☺☺
Run 39 *	3.412	3.346	3.259	3.565	-2%	☺☺

Runs indicated with * indicate test runs with additional variation in the other variables next to ISA, Ca or Cl.

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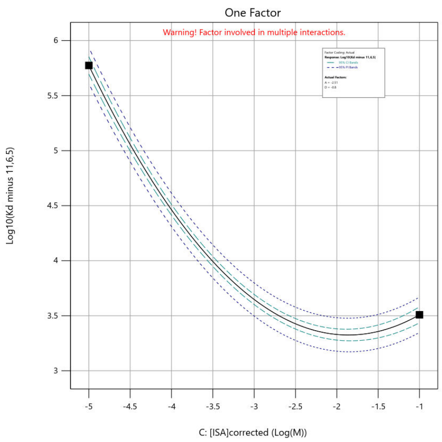
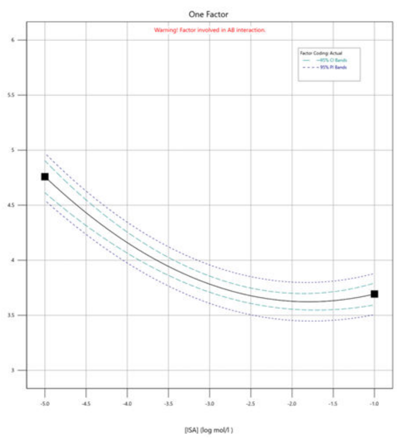
Comparission with previous model





New model @
Cl = 158 mmol/l
Ca = 3.1 mmol/l

Initial model @
Cl = 158 mmol/l
Ca = 3.1 mmol/l

As indicated previously the intial model seems to underestimate sorption, especially at the low ISA-concentrations, below 10^{-4}M, compared to new model.

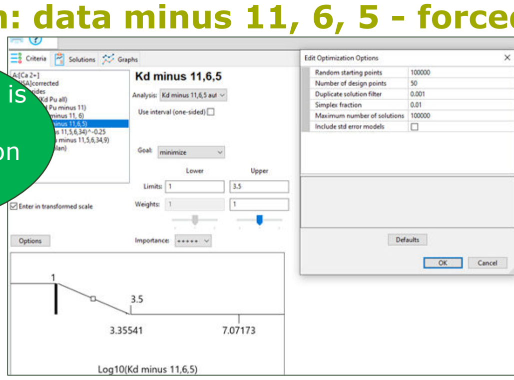
In any case, both models are in good agreement for ISA concentration > 10^{-4} M.

In future R&D either we must limit our window to ISA>ca.10^{-4} M or we must invest to increase reliability of measurements at high Rd.

Case study: Pu sorption: the sequel

Exploitation: data minus 11, 6, 5 - forced st. dev

" Now tell me, what is the lowest possible Rd in the conf. region for [Ca] "



Solutions

32057 Solutions found

Number	[Ca 2+]	[ISA]	[ISA]corrected	Chlorides	Log_{10}(Kd minus 11,6,5)
1	-2.514		-1.665	-1.691	3.017

" Assuming no block effect, 3.017 log Rd at average, with the lower level of the 95% PI at 2.837 "

" The minimum can be found
- near low [Cl] (20mM);
- and near intermediate [ISA] 20 mM;
- at upper level of the conf. region for [Ca] "

Conclusions

- Although many uncertainties were encountered, the sorption of Pu on cement could be quantified.
- Unexpected influencing factors and interactions could be detected and coped with.
- Additionally, although DoE, asks for prior reflections, it is flexible, and an existing research can be steered to address new insight or questions.