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# Conditioning of Radioactive Waste by Homogenous Cementation

Erik Coppens

21st Exchange Meeting ESV EURIDICE GIE

29/05/2017

Belgian Agency for Radioactive Waste and Enriched Fissile Materials

## Conditioning of Radioactive Waste by Homogenous Cementation

- Introduction
- The challenges and their origine
- How to develop a cemention process
- Conclusion

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## Conditioning of Radioactive Waste by Homogenous Cementation - Introduction

Conditioning are those operations that produce a waste package suitable for handling, transport, storage or disposal.

This may include solidifaction, the conversion of a gaseous, liquid or liquid-like materials into a solid waste form, often done by homogenous intermixing with a cement

Homogenous Cementation : A conditioning process consisting of a solidification (=immobilisation) by homogenous intermixing with cement.

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## Conditioning of Radioactive Waste by Homogenous Cementation - Introduction

**Homogenous cementation**

1. (Aqueous) waste is fed
2. (gravel and sand is fed)
3. **Cement** is fed
4. (In-drum) mixing
5. (Pouring)
6. (Transport to buffer)
7. Allow for hardening
8. Transport to storage

Photo: Westinghouse

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## Conditioning of Radioactive Waste by Homogenous Cementation - Introduction

**Low-cost**
**Low-temperature**
**Mechanical strength**
**Compatible w aqueous flux**
**Elevated pH**

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## Conditioning of Radioactive Waste by Homogenous Cementation - Introduction

Low-cost
Low-temperature
Mechanical strength
Compatible w aqueous flux
Elevated pH

It looks simple, but it isn't

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## Conditioning of Radioactive Waste by Homogenous Cementation

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## Homogenous Cementation – The Challenge

1. (Aqueous) waste is fed
2. (gravel and sand is fed)
3. Cement is fed
4. (In-drum) mixing
5. (Pouring)
6. (Transport to buffer)
7. Allow for hardening
8. Transport to storage

At all these (intermediate) process-steps the waste form should be compatible with the technical installation and in compliance with the waste acceptance criteria.

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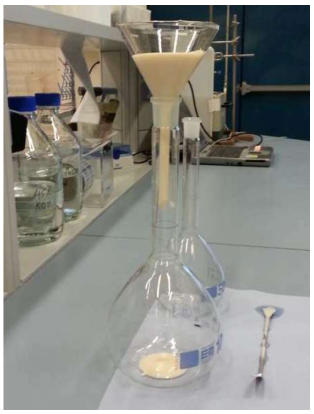
## Homogenous Cementation – The Challenge

1. **(Aqueous) waste is fed**
2. (gravel and sand is fed)
3. Cement is fed
4. (In-drum) mixing
5. (Pouring)
6. (Transport to buffer)
7. Allow for hardening
8. Transport to storage

Example: The waste is (after pretreatment) difficult to feed.



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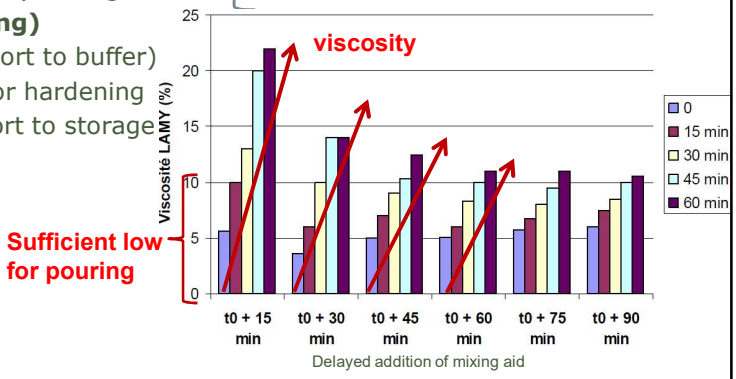
## Homogenous Cementation – The Challenge

1. (Aqueous) waste is fed
2. (gravel and sand is fed)
3. Cement is fed
4. (In-drum) mixing
5. **(Pouring)**
6. (Transport to buffer)
7. Allow for hardening
8. Transport to storage

Example: viscosity of the mixture is rising fast, not allowing for pouring.

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## Homogenous Cementation – The Challenge

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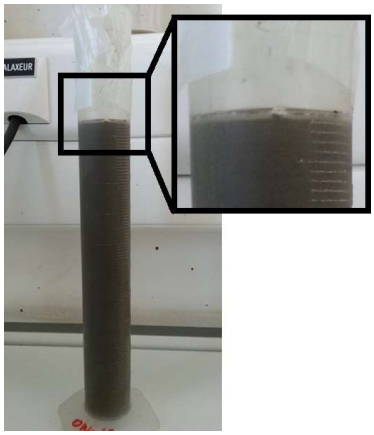
4. (In-drum) mixing
5. (Pouring)
6. **(Transport to buffer)**
7. Allow for hardening
8. Transport to storage

Example: The waste form is unstable during setting from a rheological point of view.



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## Homogenous Cementation – The Challenge

1. (Aqueous) waste is fed
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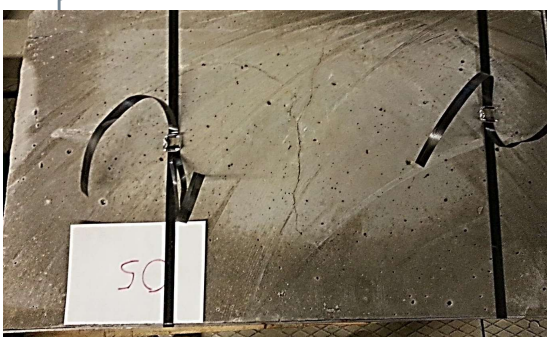
3. Cement is fed
4. (In-drum) mixing
5. (Pouring)
6. (Transport to buffer)
7. **Allow for hardening**
8. Transport to storage

Example: The waste form is cracked and fissured due to hydration heat.

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## Homogenous Cementation – The Challenge

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5. (Pouring)
6. (Transport to buffer)
7. Allow for hardening
8. Transport to **storage**

Example: The waste form suffers from a pathology.

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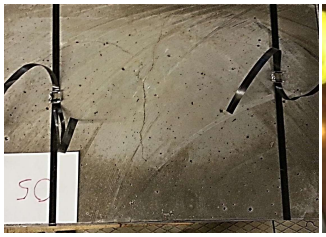
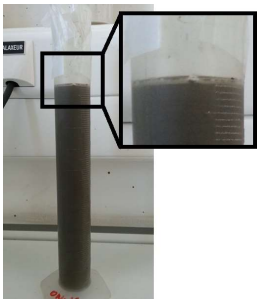
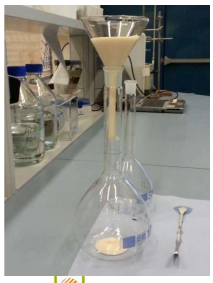
## The Origine of Challenges

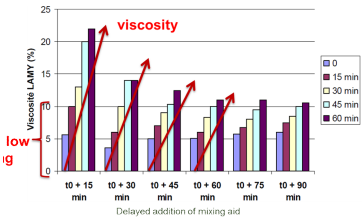






**None of these problems is related to radioactivity.**

**Classic chemistry is dominating the behavior.**

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## The Origine of Challenges

### How come these problems are (often) unforeseen?

Knowledge of the effect of mixing cement(s) with concentrates of complex chemistry is still limited.

1. Most available data on the interaction of salts with cement are relative to each species taken separately from the others. Although interactions, synergy and antagonism exists.

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   **Example: Compressive strength of waste form – contour plots**

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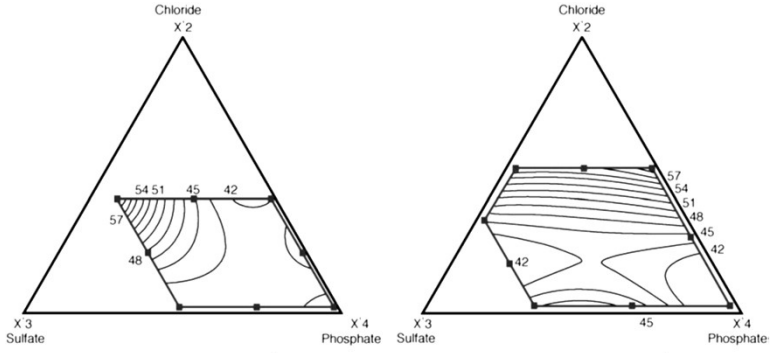
## The Origine of Challenges

### Example: interaction

(from C. Cau-dit-Coumes, S. Courtois / Cement and Concrete Research 33 (2003) 305-316)

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   **Example: The effect of phosphate on the hydration kinetics of Portland cement.**

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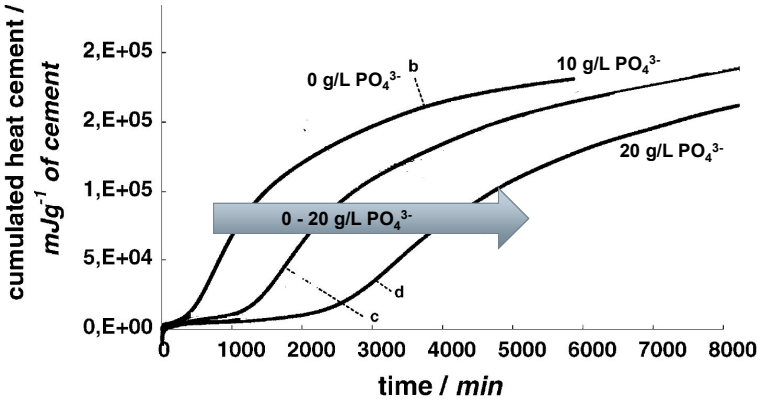
## The Origin of Challenges

**Example: phosphates – concentration effect**

(from P. Bénard, S. Garrault, A. Nonat and C. Cau-dit-Coumes
Journal of the European Ceramic Society 25 (2005) 1877–1883 )

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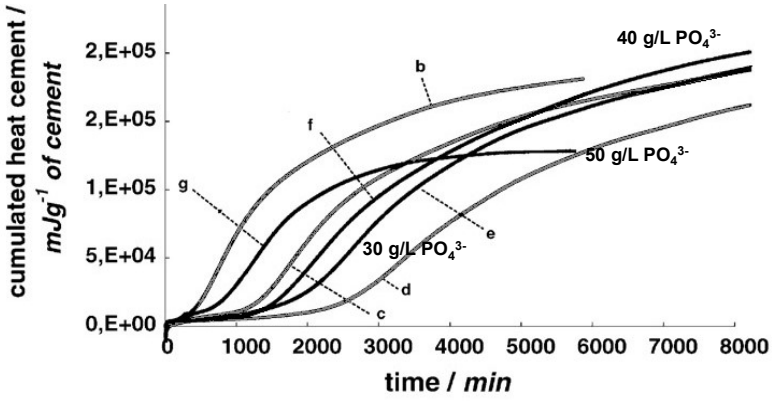


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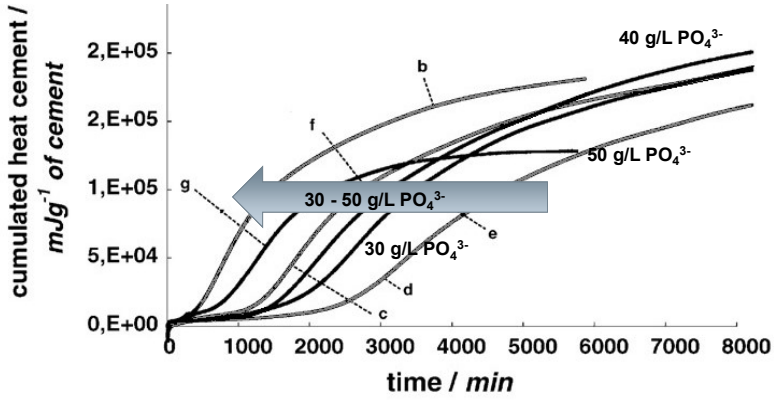


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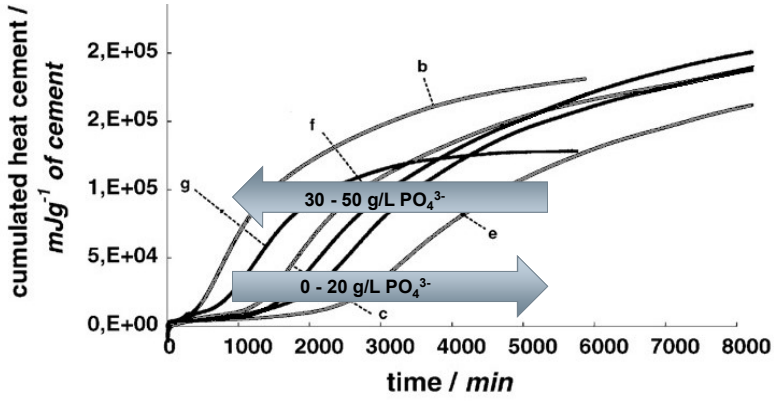


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1. Most available data on the interaction of salts with cement are relative to each species taken separately from the others. Although interactions, synergy and antagonism exists.
2. Unexpected concentration effects are sometimes observed.
3. The system itself is not constant. Waste composition can vary in function of time, batch by batch, affecting the behavior of the (intermediate) waste forms. **Example: the concept of a waste domain.**

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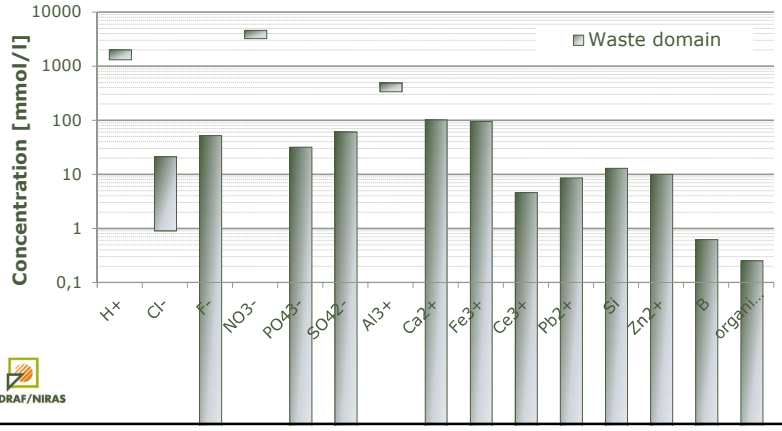
## The Origin of Challenges

### Example: Waste domain – variation in brute waste

(from E. Coppens, P. Antonucci and C. Cau-dit-Coumes
WM2016 Conference, March 6-10, 2016, Phoenix, Arizona, USA.)

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4. Unexpected kinetic effects are sometimes observed. **Example: pretreatement of acidic waste before cementation.**

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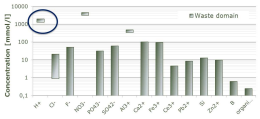
## The Origin of Challenges




### Example: Pretreatement of the waste - Kinetic effects

Raw waste + base → towards cementation

Day after

→ After the weekend

→ After the prolonged weekend

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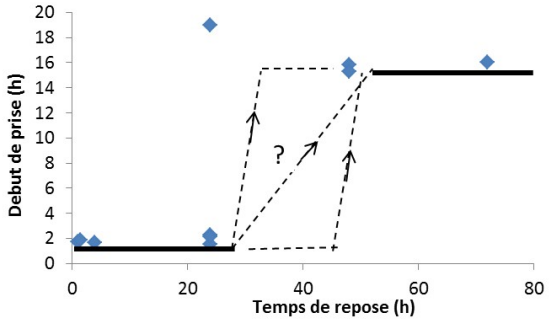
## The Origin of Challenges

### Example: Pretreatment of the waste before cementation

Raw waste + base → towards cementation




(from CEA O/N-BP R&D on homogenous cementation)

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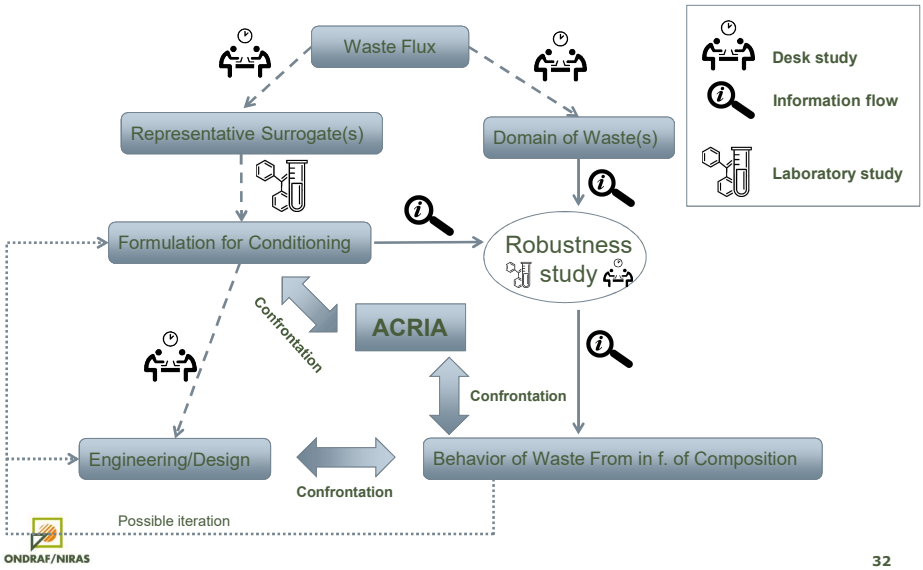
## How to approach the developpement of a Homogenous Cementation Process

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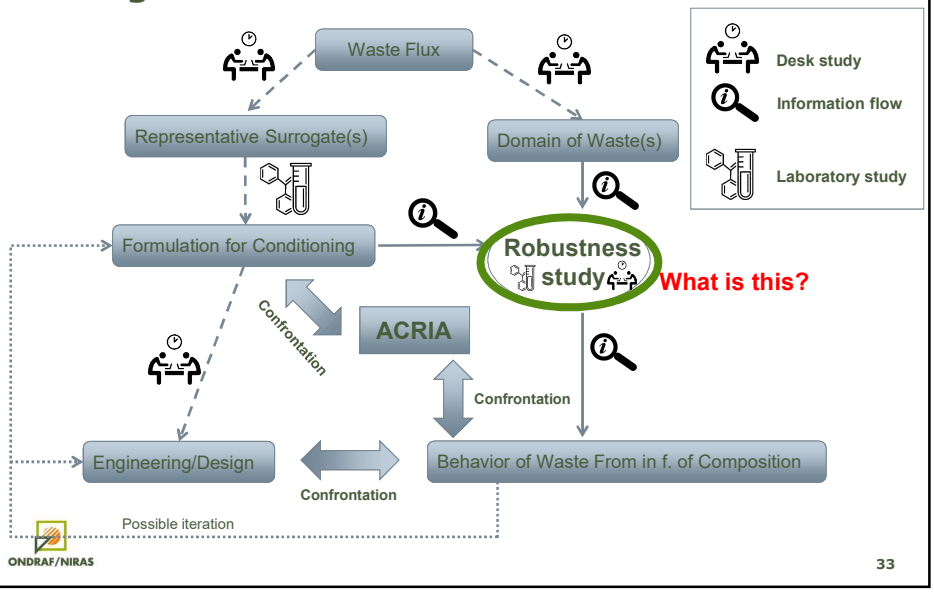
## How to approach the developpement of a Homogenous Cementation Process

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## Robustness Study

**Checking the whole waste domain** for incompatibilities by making use of non-radioactive **surrogates**.

**Often proposed approaches**
- **Intuitive approach**
- **Study by changing one factor at a time**

**Preferred approach**
- **By DOE 'Design Of Experiments'**

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## Robustness Study

**Checking the whole waste domain** for incompatibilities by making use of non-radioactive **surrogates**.

Often proposed approaches
- Intuitive approach
- Study by changing one factor at a time

**Preferred approach**
- **By DOE 'Design Of Experiments' in two stages**
  1. Identification of the **main influencing species** within the domain of study
  2. A surface response investigation, focused on the main influencing species to **build predictive models for predicting properties** of the cement-waste form as function of the waste composition.
     - to confront with imposed criteria
     - To confront with engineering / design

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## Robustness Study

Desk study

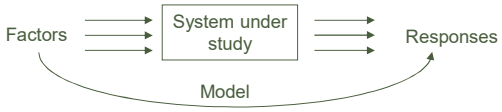
Laboratory study

**Main Principles of Design Of Experiments (DOE)**

**1. Defining your objective**

Screening ⇨ Study of interactions ⇨ Surface-response Study ⇨ Multi-criteria optimisation

**2. Define factors, experimental domain, and responses**




**3. Choose a model**
- **Empirical**
- **In function of your objective**

| Objective | Postulated model |
|---|---|
| Screening | $\eta = \beta_0 + \sum_{i=1}^{k} \beta_i x_i$ |
| Study of Interactions | $\eta = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j$ |
| Surface Response Study | $\eta = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2$ |

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## Robustness Study

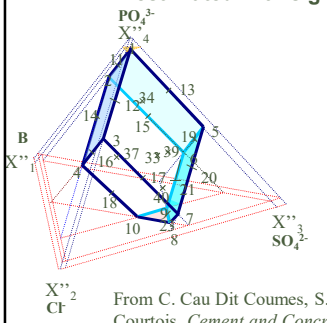
Desk study

Laboratory study

### Main Principles of Design Of Experiments (DOE)

**4. Choosing the experimental matrix.**

The experiments must be chosen / localized in the domain of interest (*the waste domain*) in such a way the coefficients of the imposed models can be estimated with significant confidence.




From C. Cau Dit Coumes, S. Courtois, *Cement and Concrete Research*, **33 [3]** (2003) 305-316

**5. Realization of the experiments.**

**6. Calculation of the estimates for the models coefficients.**

**7. Validation of the model.**

**8. Interpretation of the results.**

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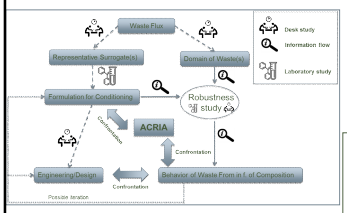
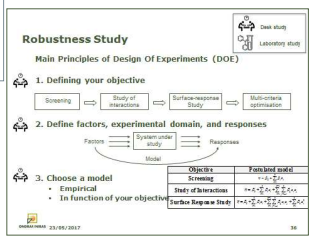
## Conclusion

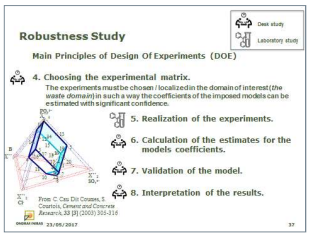
**Main problem:** Knowledge of the effect of mixing cement with concentrates of complex chemistry is very limited

**Thus:** Cementation might look easy, it is not.

**However:** A well thought-trough approach allows for developing cementation processes in a rigid way.

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