Conditioning of HA/ILW, statistical approach of glass formulation and property modeling

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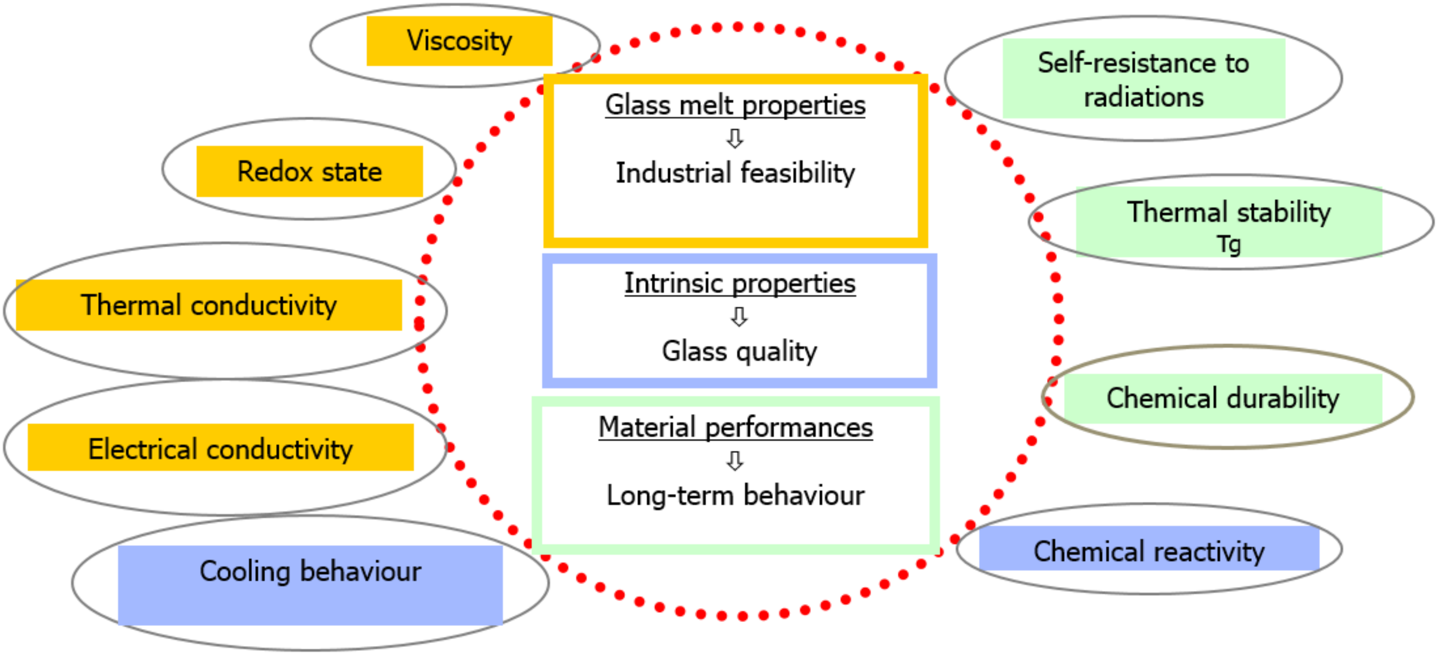
ICTP/IAEA Summer School, Trieste sept 2019

COURSE OBJECTIVES

Give students and young researchers in nuclear waste vitrification:

- Basics on statistical modeling in formulation
  - Design of experiments, mixture designs
- Brief description of possible approaches for glass property modeling
- Statistical approach applied to waste with high variability of composition
- Knowledge on database and Machine Learning for property prediction
  - Application examples using Neural Nets in glass science
- Information on where to find glass property data

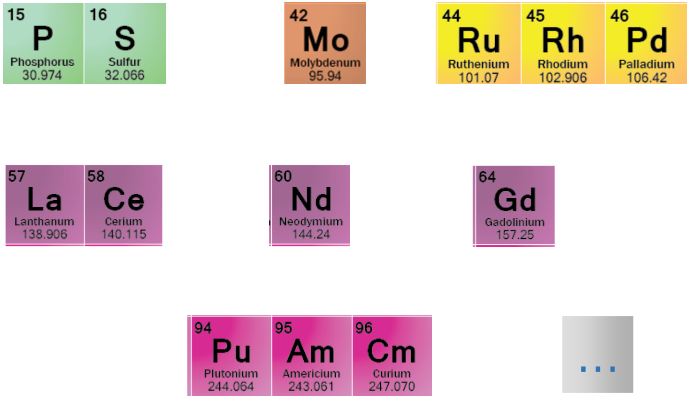
NUCLEAR GLASS FORMULATION CHALLENGES



Composition of the reference Fission Product solution (R7T7, France)	
Teneur des éléments (en g/L) pour 711 L/tU (1)	
Na	14,09
Al	3,52
P	0,51
Cr, Fe, Ni	11,22
Rb	0,50
Sr	1,18
Y	0,65
Zr	6,48
Mo	4,70
Tc	1,16
Ru, Rh, Pd	5,48
Ag, Cd, Sn, Sb, Se	0,38
Te	0,67
Cs	3,72
Ba	2,21
La	1,70
Ce	3,30
Pr	1,56
Nd	5,63
Pm	0,10
Sm	1,12
Eu	0,18
Gd	0,11
U	0,11
Pu	0,00
Am, Cm, Np	1,08

Finding the appropriate glass formulation is very challenging:

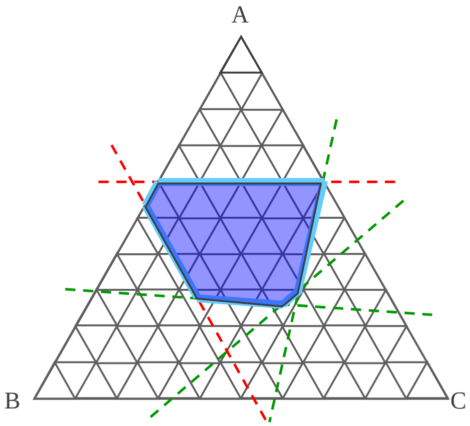
- ➢ number of different radioelements in the waste
- ➢ low solubility of some of these elements in sodium borosilicate glass

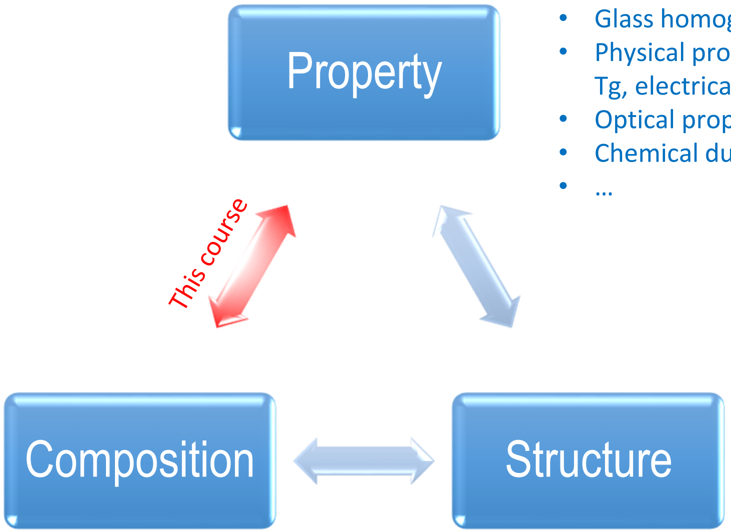


Problematic

Chemical composition range of R7T7 glasses produced in the AREVA - La Hague plant workshops			
Oxides	Specified interval for the industry (wt%)		Average composition of industrial glasses (wt%)
	min	max	
SiO_2	42.4	51.7	45.6
B_2O_3	12.4	16.5	14.1
Al_2O_3	3.6	6.6	4.7
Na_2O	8.1	11.0	9.9
CaO	3.5	4.8	4.0
Fe_2O_3		< 4.5	1.1
NiO		< 0.5	0.1
Cr_2O_3		< 0.6	0.1
P_2O_5		< 1.0	0.2
Li_2O	1.6	2.4	2.0
ZnO	2.2	2.8	2.5
Oxides (PF + Zr + actinides) Fines suspension	7.5	18.5	17.0
Actinide oxides			0.6

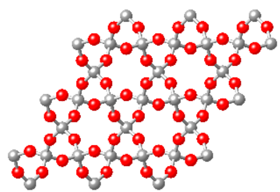
Evaluate glass properties (homogeneity, physical and chemical properties) at any point in the composition domain





- Glass homogeneity
- Physical properties: viscosity, density, Tg, electrical conductivity,…
- Optical properties
- Chemical durability
- …

Oxides	Composition (wt. (%))SiO_2
SiO_2	59.39
Al_2O_3	13.57
ZrO_2	15.61
Li_2O	8.64
K_2O	0.31
Na_2O	0.70
TiO_2	0.09
Fe_2O_3	0.22
CaO	0.62
P_2O_5	0.82



Three approaches to model a property

- Theoretical, cognitive approach

Based on our intrinsic knowledge of the phenomenon, on the fundamental laws of physics and chemistry (conservation of energy, momentum, equations of diffusion, thermodynamics,…)

- Empirical approach

Based on a set of experimental data (*data-driven* models). Mathematical, statistical approach, which ignores any physicochemical knowledge of the phenomenon

- Mixed approach

Combination of the two previous approaches

- For these three classes of models, there are different types: linear or non-linear, static or dynamic, deterministic or stochastic, continuous or discrete,…

Theoretical Principle of Additivity

M.B. Volf, "Mathematical Approach to Glass", Elsevier Science Publishing company, 1988

- If glass were a simple mixture of the individual oxides, the **additive equation** would be generally valid:

$$G = \sum g(G)_i \, x_i$$

G is the property of the glass
$g(G)_i$ is the additive factor for oxide i and property G
x_i is the amount of oxide i

- But glass is not a mixture of oxides... Errors in additive calculation could be due to the degree of cross-linking, anomalies in the cross-linked structure, phase separation, interaction between ions,...
- However, on investigating a suitably narrow composition range, where the more complex interactions can be neglected, **one can express the effect of the individual components on a certain property by the additive equation.**

Statistics for glass formulation:

The design of experiments methodology

- Scientific experiments involve three stages:
  - Stage 1 - Planning of the experiment
  - Stage 2 - Achievement of the experiment
  - Stage 3 - Analysis and interpretation of the data
- When **statistical principles** are applied during this process, the methodology is called « **Design of Experiments (DOE)** » or « **Experimental designs** »
- DOE involves **factors** and **response(s)**
  - **Response(s) = *f* (factor levels)**

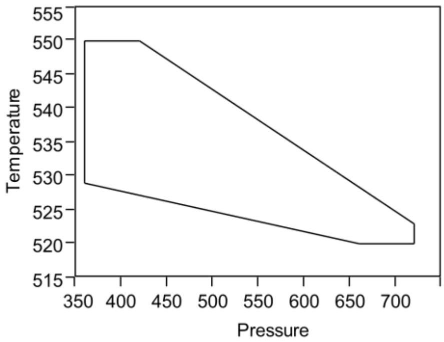
  Where f is a mathematical function of the levels of a factor (f can be the equation of Additivity for example)
- A "mixture design" is a DOE for mixture (= formulation) studies

Stage 1: Planning of the experiments

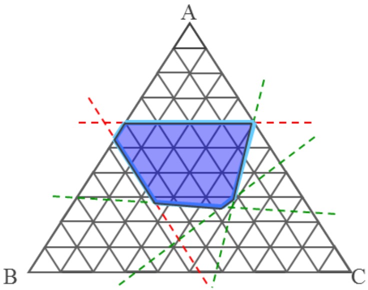
- **Precisely** define the objectives of the study
  - Either: identify factors influencing a response (screening design)
  - Or: make prediction or optimization (response surface methodology)

Stage 1: Planning of the experiments

- Define the experimental domain
  - Factors
  - Boundaries



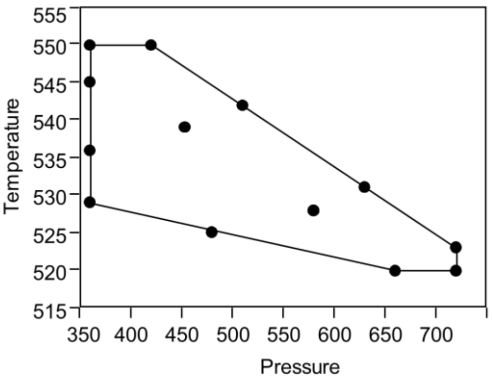
« Process » design

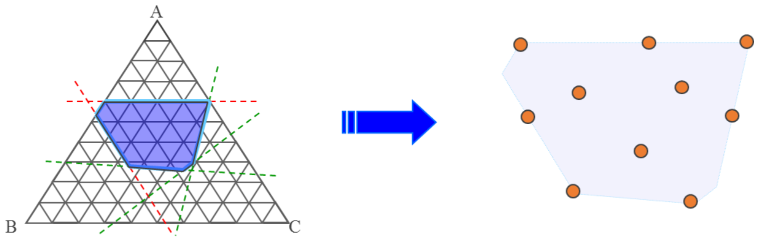


« Mixture » design

Stage 1: Planning of the experiments

- Build the DOE (= define experiments to be achieved)
  - Optimality criteria (D-opt, I-opt,…)
  - Commercial software for DOE construction JMP, Design Expert, Minitab,…





Stage 1: Planning of the experiments

Example of experimental constrained domain

Chemical composition range of R7T7 glasses produced in the AREVA - La Hague plant workshops			
Oxides	Specified interval for the industry (wt%)		Average composition of industrial glasses (wt%)
	min	max	
SiO_2	42.4	51.7	45.6
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Na_2O	8.1	11.0	9.9
CaO	3.5	4.8	4.0
Fe_2O_3		< 4.5	1.1
NiO		< 0.5	0.1
Cr_2O_3		< 0.6	0.1
P_2O_5		< 1.0	0.2
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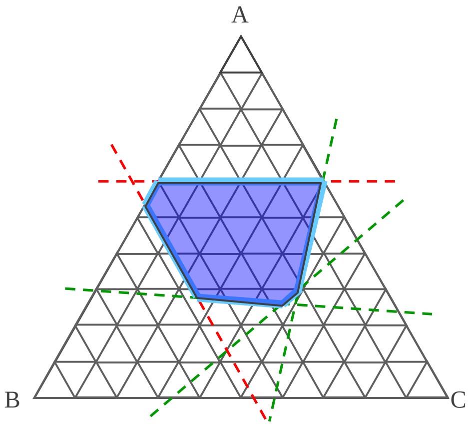
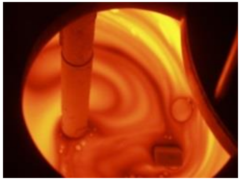


individual constraints

relational constraints

Stage 2: Make the experiments



Exp. No.	SiO_2	B_2O_3	Na_2O	Li_2O	Al_2O_3	CaO	La_2O_3
G-1	42.0	23.3	4.0	0.0	20.0	2.7	8.0
G-2	42.0	14.9	5.0	2.1	20.0	8.0	8.0
G-3	55.0	14.0	4.0	0.0	13.1	5.9	8.0
G-4	48.7	14.0	4.0	1.7	20.0	8.0	3.6
G-5	55.0	21.0	7.1	0.0	12.0	2.0	2.9
G-6	42.0	17.4	12.0	0.0	18.6	2.0	8.0
G-7	42.0	19.6	12.0	0.0	20.0	3.1	3.3
G-8	47.9	14.0	9.9	3.0	20.0	2.0	3.2
G-9	55.0	23.0	4.0	0.0	12.0	2.0	4.0
G-10	55.0	14.0	5.5	2.4	13.1	2.0	8.0
G-11	42.0	30.0	4.2	1.8	12.0	2.0	8.0
G-12	42.0	30.0	6.0	2.6	14.1	2.0	3.3
G-13	49.0	16.3	4.0	0.7	20.0	2.0	8.0
G-14	42.0	26.8	4.0	0.0	15.9	8.0	3.3
G-15	46.8	19.7	6.0	1.0	16.8	3.8	5.8
GV-1	55.0	14.0	7.9	0.0	13.1	2.0	8.0
GV-2	42.0	23.3	8.8	0.0	15.2	2.7	8.0
GV-3	42.0	27.0	4.0	0.0	13.1	5.9	8.0
GV-4	42.0	19.6	4.0	0.0	20.0	6.4	8.0
GV-5	42.0	26.8	4.0	0.0	15.9	3.3	8.0
GV-6	45.0	20.2	4.0	1.7	17.5	4.6	7.0

V. Piovesan et al. ; J. of Nuclear Materials ; 483 (2017) 90-101

Stage 3: Statistical analysis of the results

- Response distribution and variance
- Comparison with the experimental error

Exp. No.	SiO_2	B_2O_3	Na_2O	Li_2O	Al_2O_3	CaO	La_2O_3
G-1	42.0	23.3	4.0	0.0	20.0	2.7	8.0
G-2	42.0	14.9	5.0	2.1	20.0	8.0	8.0
G-3	55.0	14.0	4.0	0.0	13.1	5.9	8.0
G-4	48.7	14.0	4.0	1.7	20.0	8.0	3.6
G-5	55.0	21.0	7.1	0.0	12.0	2.0	2.9
G-6	42.0	17.4	12.0	0.0	18.6	2.0	8.0
G-7	42.0	19.6	12.0	0.0	20.0	3.1	3.3
G-8	47.9	14.0	9.9	3.0	20.0	2.0	3.2
G-9	55.0	23.0	4.0	0.0	12.0	2.0	4.0
G-10	55.0	14.0	5.5	2.4	13.1	2.0	8.0
G-11	42.0	30.0	4.2	1.8	12.0	2.0	8.0
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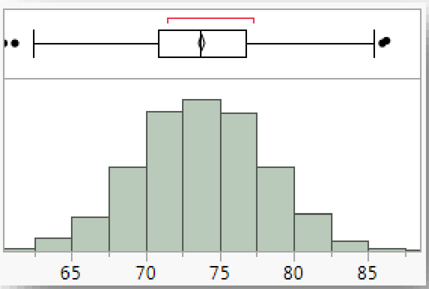
GV-5	42.0	26.8	4.0	0.0	15.9	3.3	8.0
GV-6	45.0	20.2	4.0	1.7	17.5	4.6	7.0

Response



Measured Property Distribution

Stage 3: Statistical analysis of the results

- Determination of the factors having a significant effect on the response variation
- Create mathematical models using multilinear regression

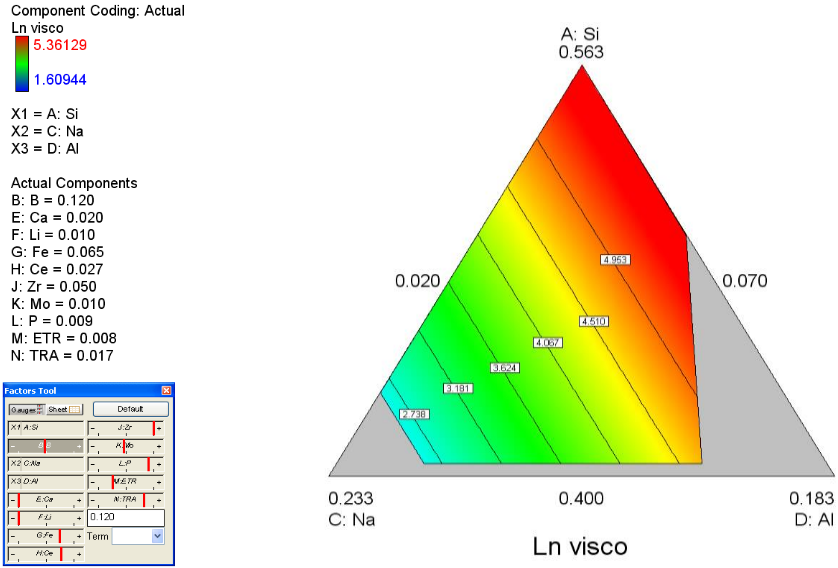
Response(s) = *f* (factor levels)

$$\hat{y}_i = \sum_{i=1}^{q} a_i x_i + \sum_{i=1}^{q-1} \sum_{j=i+1}^{q} a_{ij} x_i x_j$$

The model enables to predict the property **for any composition inside the experimental domain**

Stage 3: Statistical analysis of the results

- Use the mathematical model to explore the experimental domain



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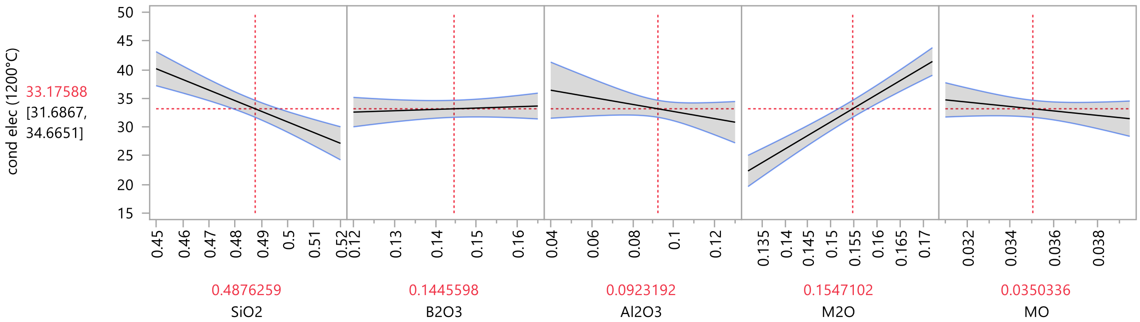

Stage 3: Statistical analysis of the results

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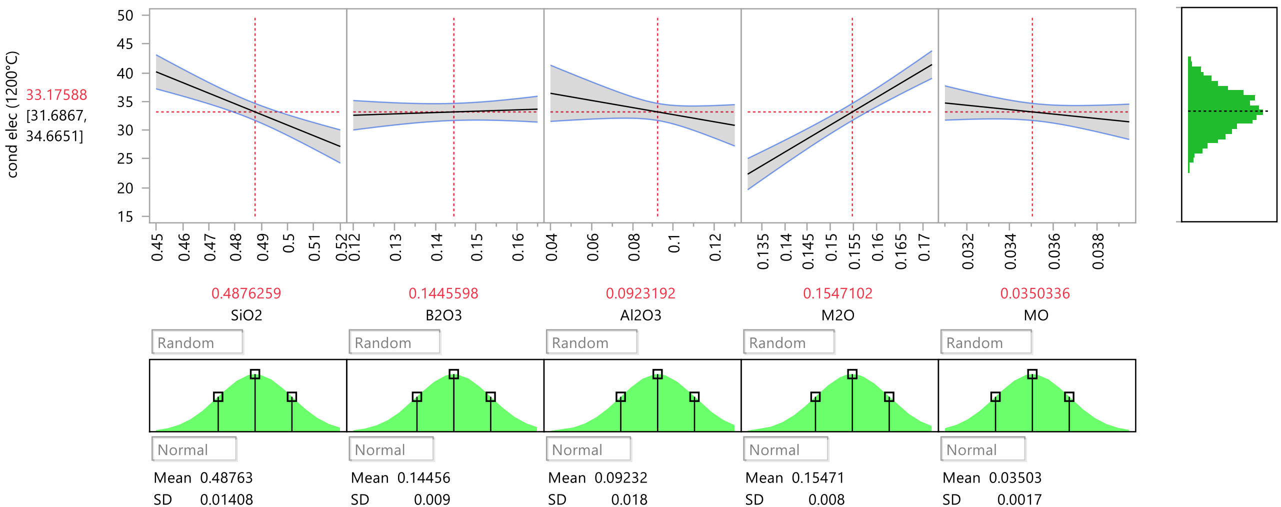
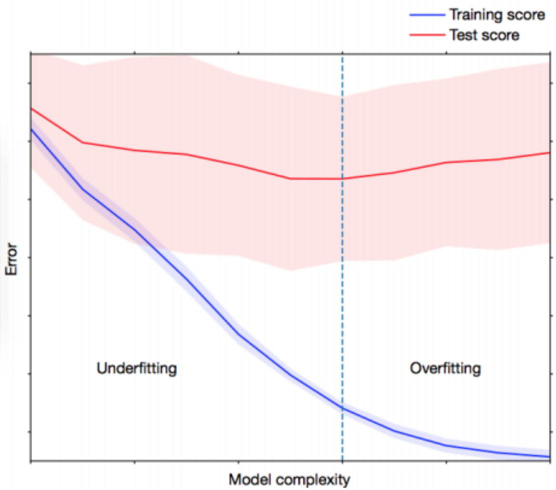


Advice when running a study with a DOE approach

- Define a clear objective
- Make sure to identify all possible effects
- Define appropriate range of variation (min-max) for the effects
- Take into account strong interactions if known
- How many runs?
  - In many cases it is better (faster and cheaper) to run two DOEs instead of one
  - Take time to create, evaluate and compare several DOEs
- **Validate your models** with additional experiments

Advice when building predictive models

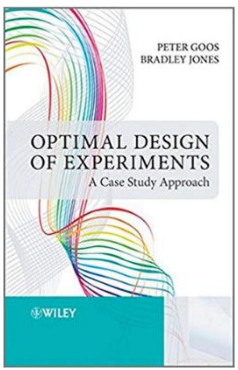
- Beware of overfitting (principle of parsimony)

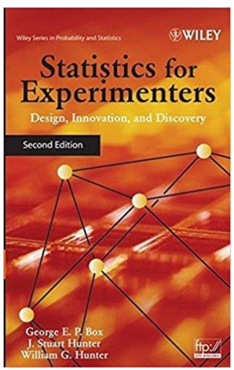


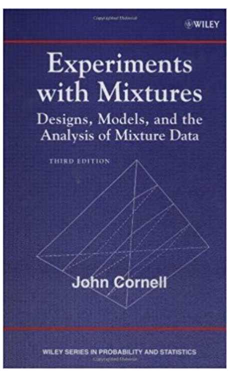
from K. T. Butler et al. *Machine learning for molecular and materials science*
Nature, 2018

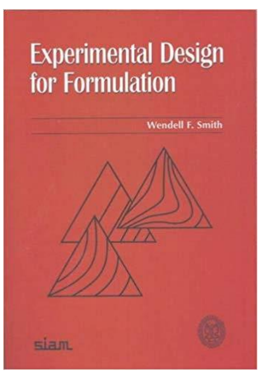
Conclusion of the Design of Experiments approach

- DOE methodology is very robust for statistical property prediction on **small domains of composition**
- Polynomial models obtained from multilinear regression are simple and easy to use
- To go further:









Statistics for glass formulation:

Database and machine learning

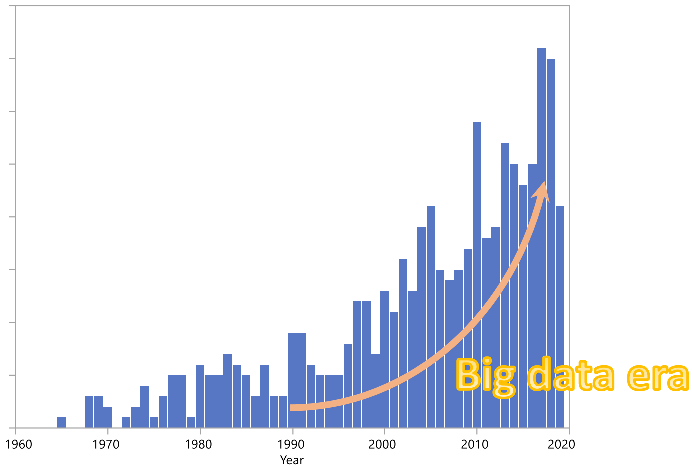
Available resources in glass science and technology

- First attempt for the calculation of glass properties from their composition proposed by Winckelmann and Schott at the end of the 19th century
- Monograph by Volf in 1988 that describes best known methods [1]
- Since 1988 methods have been proposed for viscosity calculation (Lakatos, Lyon, Mazurin, Hrma, Priven, Okhotin, Fluegel,…)

[1] Mathematical approach to glass. by *M. B. Volf*. Elsevier Science Publishers, Amsterdam (1988)

Available resources in glass science and technology

Published literature in the field of glass property prediction

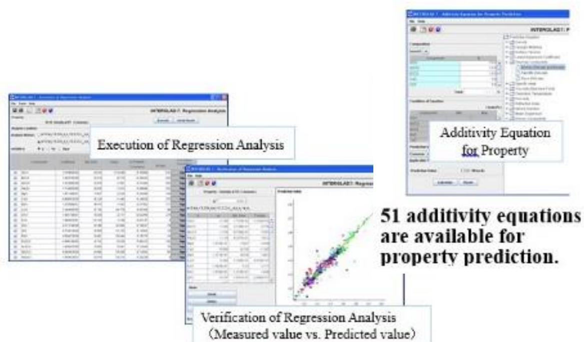


From Web of Science
« glass » and « prediction » in publication title

1930-60s	1970s	1980s	1990s	2000s	2010s
octets	Ko	Mo	Go	To	Po
N~10	N~100 *First PCs*	*AI, ANN*	*Big Data*		

Available resources in glass science and technology

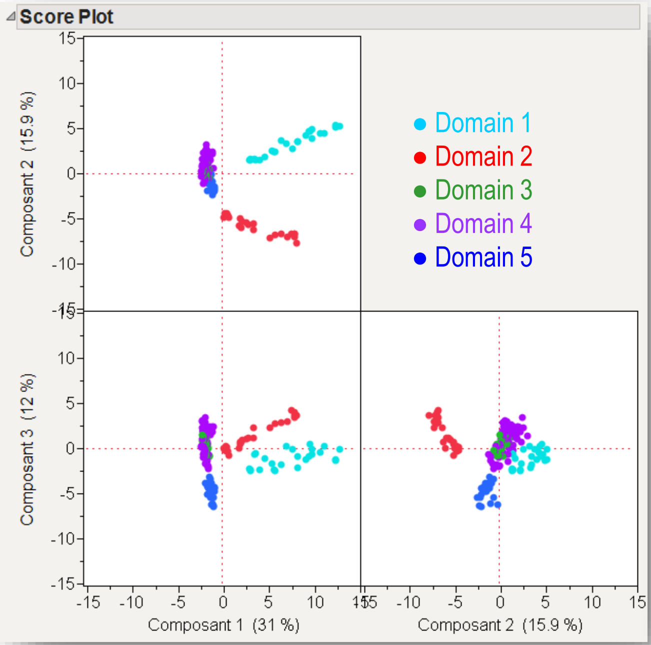
- SciGlass and Interglad Information Systems
  - Data collected from the published literature
  - Embedded property calculation tools
  - More than 300 000 glasses

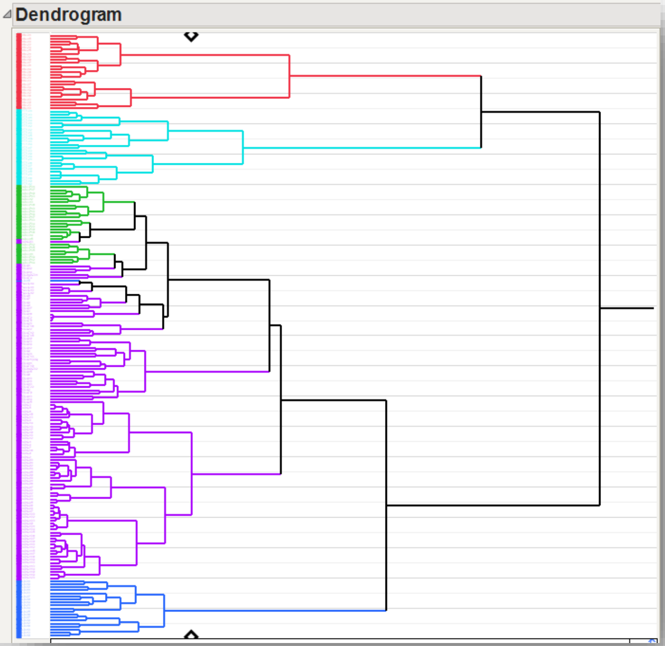


Available resources for nuclear glass property data

- Published reports from Pacific Northwest National Laboratory (PNNL)

Principal Component Analysis / Hierarchical clustering





Big Data for glass property prediction

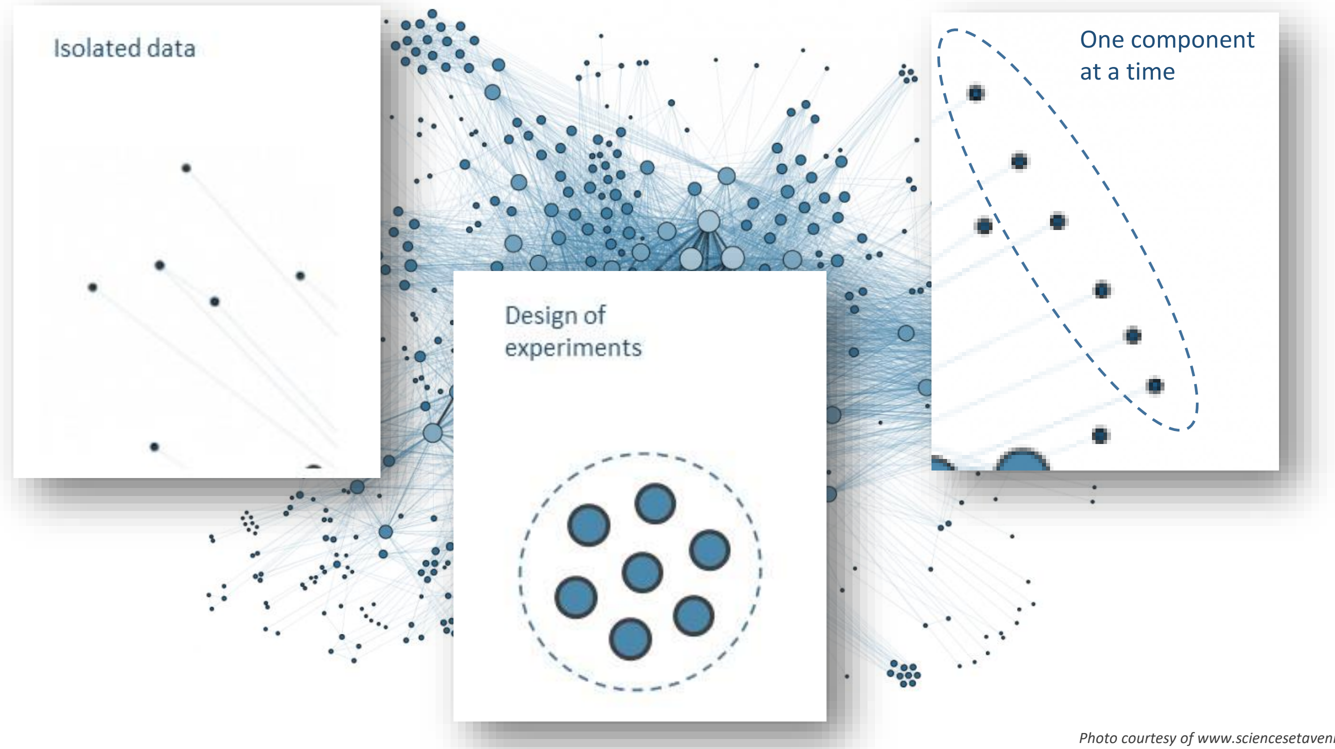
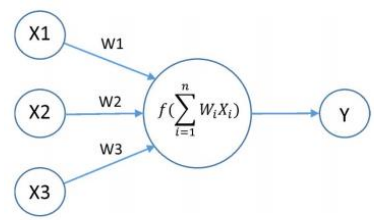
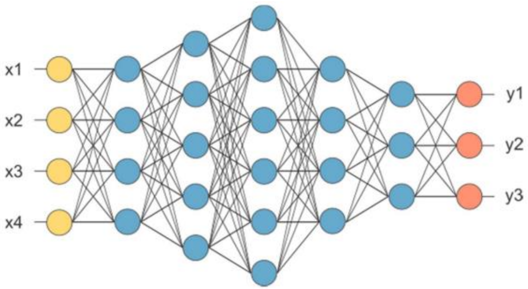


Photo courtesy of www.sciencesetavenir.fr

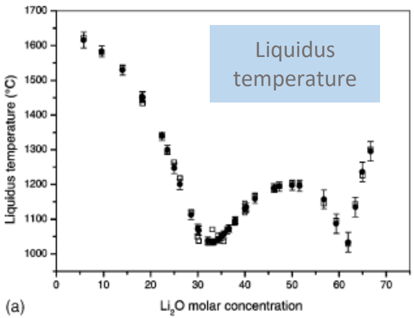
- Machine learning has seen growing application in material property determination
- Artificial Neural Networks (ANN) use interconnected mathematical nodes, or neurons, to form a network that can model complex functional relationships



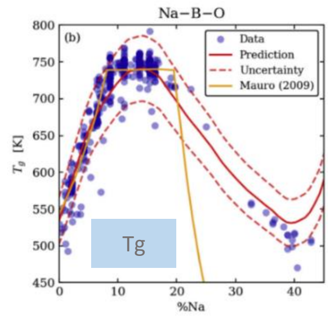


- This technique is particularly suited to problems that involve the manipulation of multiple parameters and non-linear interpolation

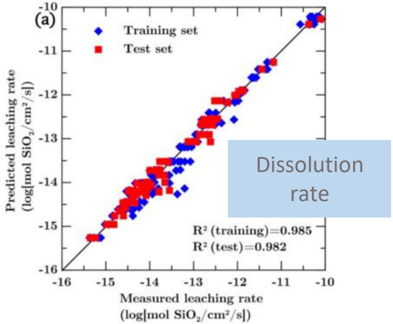
Examples of NN application to glass property prediction



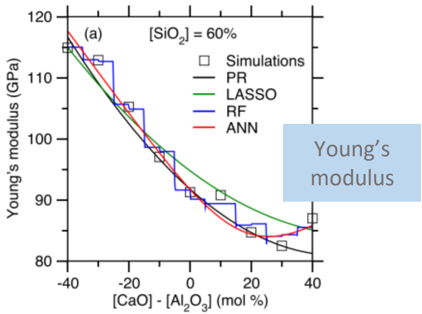
C. Dreyfus, G. Dreyfus / Journal of Non-Crystalline Solids 318 (2003) 63–78



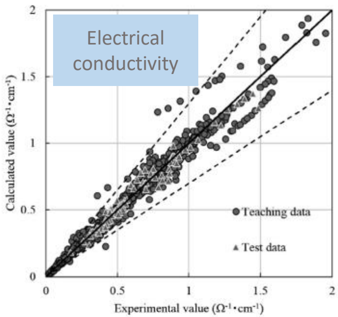
D.R. Cassar et al., Acta Materiala, 159 249-256 (2018)



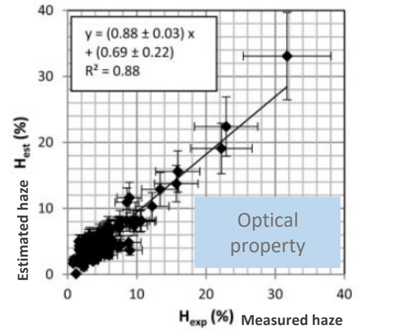
N.M. Anoop Krishnan et al.
Journal of Non-Crystalline Solids 487 (2018) 37–45



K. Yang et al.., Scientific Reports, 8739, 9 (2019)



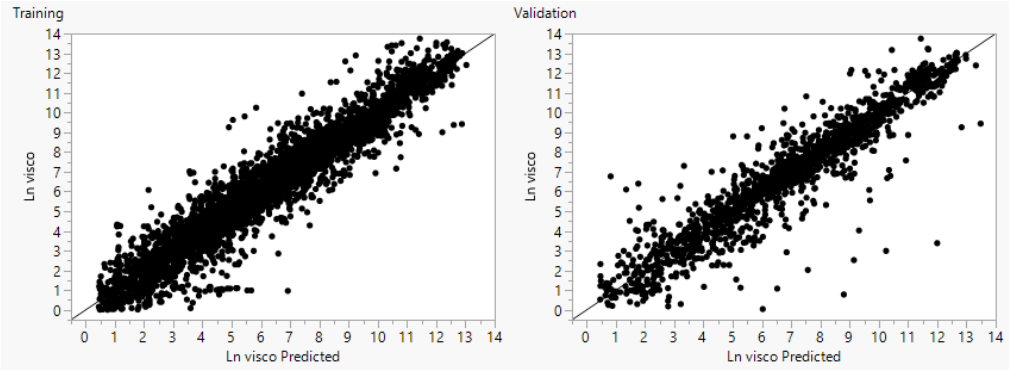
Y. Haraguchi et al., ISIJ International, Vol. 58 (2018), No. 6, pp. 1007–1012

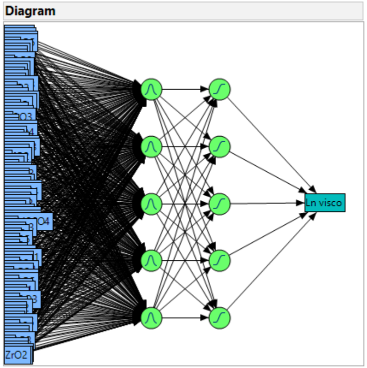


A. Verney-Caron et al., Atmospheric Environment, 54 141-148 (2012)

GLASS VISCOSITY PREDICTION

- But NN are unable to predict efficiently glass viscosity on big database…

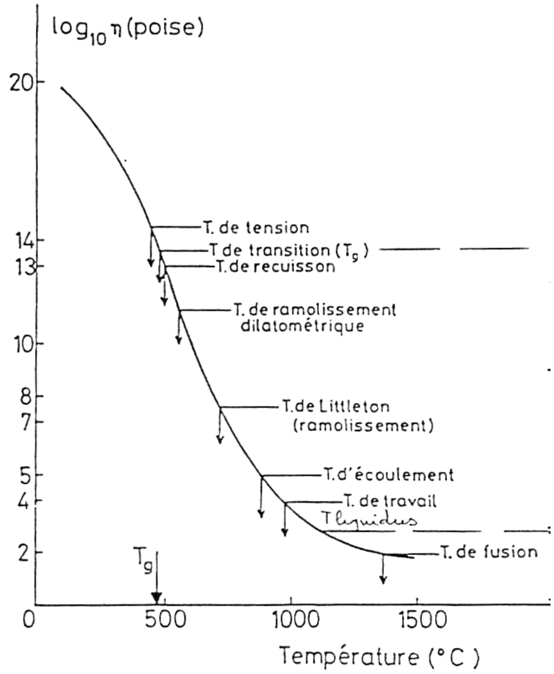




Training	
Ln visco	
Measures	**Value**
RSquare	0.9287269
RMSE	0.7518628
Mean Abs Dev	0.496624
-LogLikelihood	6435.0916
SSE	3208.6293
Sum Freq	5676

Validation	
Ln visco	
Measures	**Value**
RSquare	0.8822247
RMSE	0.9682362
Mean Abs Dev	0.5912263
-LogLikelihood	2545.9066
SSE	1721.2158
Sum Freq	1836

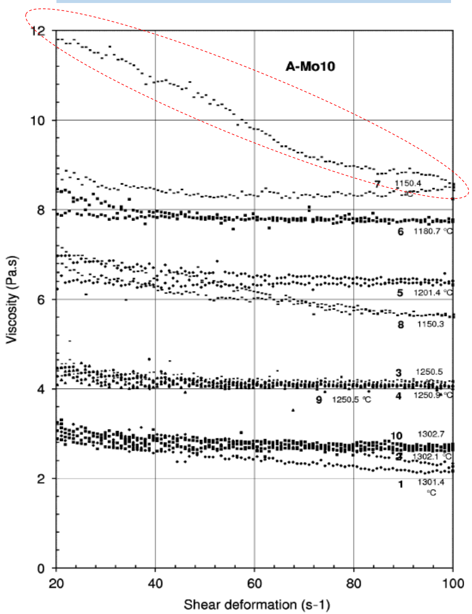
- Range of viscosity values is very wide vs temperature and vs composition



GLASS VISCOSITY PREDICTION

- Viscosity temperature dependence is highly sensitive to phase separation and crystallization

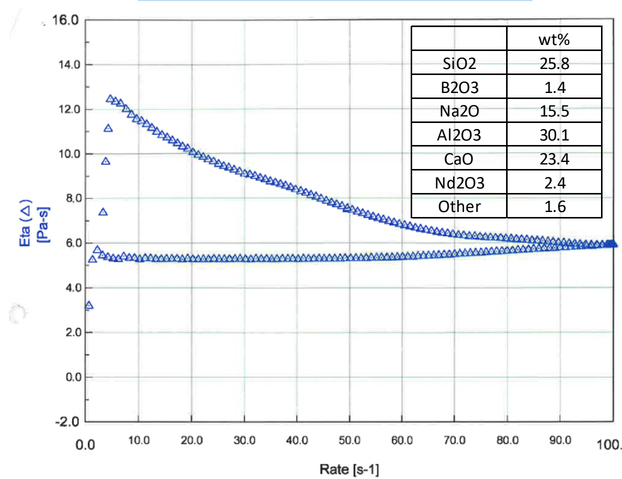
Phase separation



Oxide mol%	AMo10 batch no. 5052
SiO_2	46.5
Na_2O	11.0
B_2O_3	14.4
Li_2O	0.2
CaO	7.9
MoO_3	5.1
P_2O_5	1.6
Al_2O_3	5.4
ZnO	5.4
ZrO_2	2.0
Nd_2O_3	0.2
Minors	0.3
Sum	100.0

J. Am. Ceram. Soc., **94** [2] 447–454 (2011) –*Schuller et al.*

Crystallization



	wt%
SiO2	25.8
B2O3	1.4
Na2O	15.5
Al2O3	30.1
CaO	23.4
Nd2O3	2.4
Other	1.6

Statistics for glass formulation:

Waste with high variability of composition

Waste with high variability of composition

- Probabilistic approach applied to waste from dismantling operations

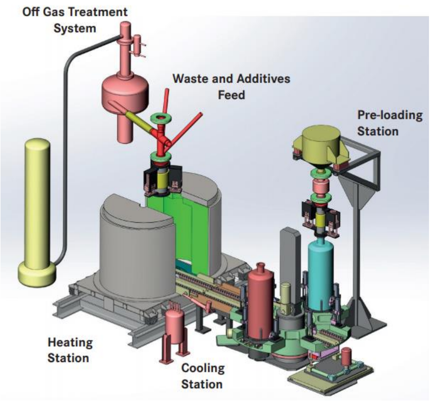
DEM'N'MELT

IN CAN vitrification for conditioning HLW/ILW-LL waste from decommissioning operations

OBJECTIVES

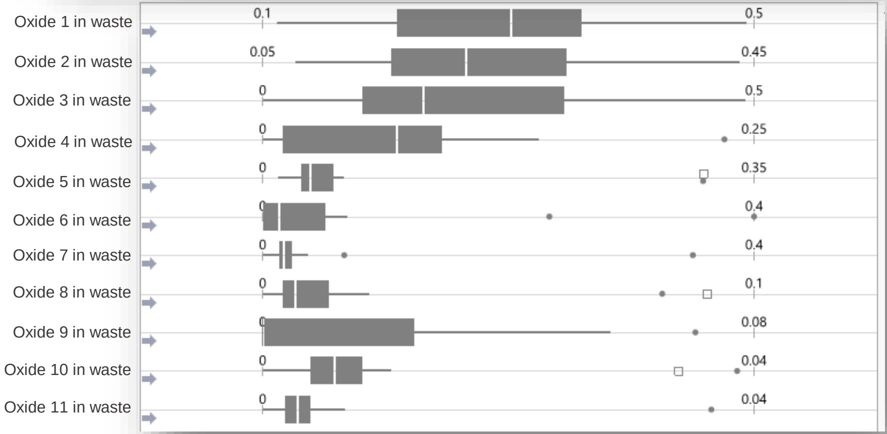
The DEM'N'MELT project seeks to develop and implement an innovative tool for high-level waste (HLW) and intermediate-level long-lived waste (ILW-LL), which:

- is sufficiently flexible to adapt to the uncertainty of the composition of waste needing processing, but which nevertheless produces waste packages whose composition, structure and radiation containment performance are properly managed for disposal;
- is based on a vitrification procedure, whereby radioactive waste is contained within glass, a material already known and used for containing high-level waste;



Waste with high variability of composition

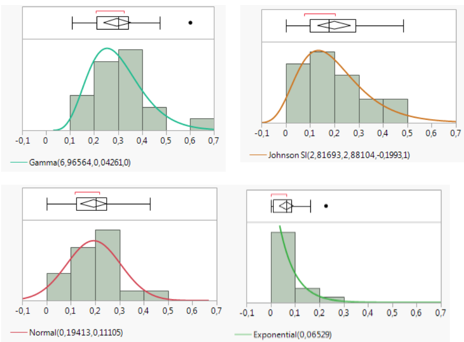
- Probabilistic approach applied to waste from dismantling operations



Waste with high variability of composition

Waste with uncertainties in composition

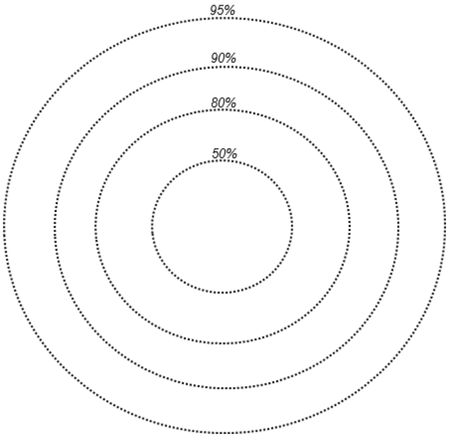
Probability functions on waste oxides contents



Glass frit

Simulation →

Glass domain of composition



⇒ Probability for an oxide to be present in the waste glass at a certain concentration

⇒ Can also be applied to linear combination, or ratio, involving several oxides

General conclusion

- When glass composition is too complex, properties can not be predicted from theoretical models
- In this case, statistical modeling using empirical data is an alternative way to predict glass properties
- Excellent predictive models can be obtained by using a Design of Experiments methodology, on small domains of composition
- Machine Learning has seen growing application in material property determination on big data sets
- Several physical and chemical glass properties can be predicted by using Neural Nets

THANK YOU FOR YOUR ATTENTION

Acknowledgments

- Glass Elaboration and Characterization teams from CEA Marcoule

V. Ansault, T. Blisson, M. Chartier, V. Debono, V. Lemaitre, S. Mure, B. Penelon, J. Renard, C. Vallat

- R&D Scientists from CEA Marcoule

J.L. Dussossoy, I. Giboire, I. Hugon, A. Laplace, M. Neyret, O. Pinet, E. Régnier, S. Vaubaillon

F. Bart, I. Bisel, C. Ladirat, S. Gin, F. Frizon, B. Lorrain

- ORANO and EDF for financial support