Coupling ICP / MS - Laser ablation relevance for prototypical Corium characterization

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COUPLING ICP/MS – LASER ABLATION : RELEVANCE FOR PROTOTYPICAL CORIUM CHARACTERIZATION

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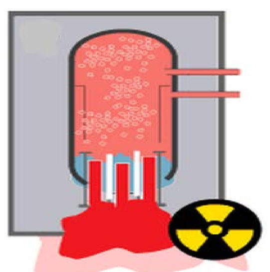
Introduction

Project background: The cooling loss of a nuclear reactor, caused by a major accident, can trigger the fusion of the core reactor and its adjacent structures.
The magma created during this fusion is named "corium" and can be responsible of the reactor tank puncture and therefore of radioactive products release related risks.

Extensive knowledge of corium ➔ **REMEDIATION AND STORAGE**

Objective : To determine the analysis optimised settings of an ablation laser coupled to an ICP/MS in order to establish the elementary and isotopic compositions of prototypical coriums.



Schema of a leaking reactor tank

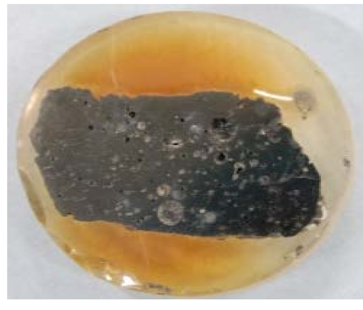
Samples

Because of its hard accessibility and its irradiations, corium samples are prototypes made from depleted uranium on CEA Cadarache site.

Fabrication steps

- Specific mixes powders (UO_2, ZrO_2, Fe_xO_y)
- Plasma arc heating in the rotary furnace of the fabrication device
- Spreading on a specific substrate tank (concrete, steel or ceramic)

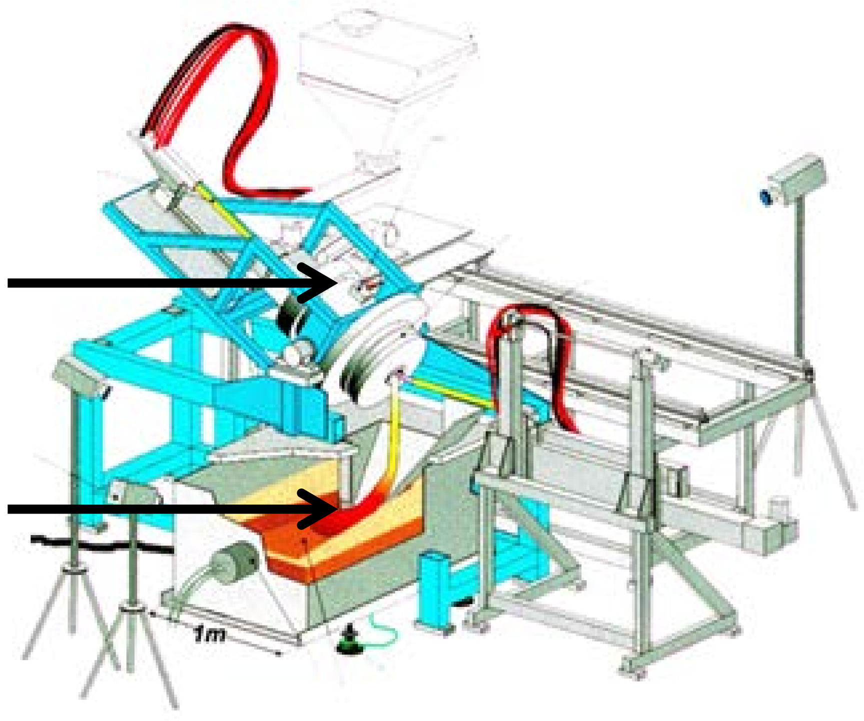
Sample preparation by resin coating then polishing



Corium prototype from Cadarache

Rotary furnace

Spreading tank



Fabrication device of corium prototypes

Analyses technique

Principle : An ablation laser is abrade the surface of the sample on some tens µm of deepth and a particles cloud is created. This spray is carried to the ICP torch by a gas mix made of helium and argon. The spray is atomized and ionized as soon as it gets in the plasma. These ions are then qualitatively and/or quantitatively analysed by the mass spectrometer. To make a more robust plasma, a second spray generated by an ultrasonic nebulizer can be added. The two particle clouds are combined using a Y-shaped piece.

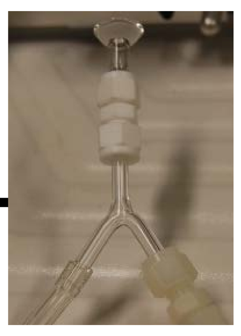
ADVANTAGES ➔ Little or no sample preparation needed and an elementary/isotopic cartography of the analysed solid can be realized.

DRAWBACK ➔ The major drawback is named « ELEMENTARY SPLITTING », which is a non-congruent ablation of the chemical elements impacting the results accuracy. This phenomenon is mainly triggered by the ablation laser caracteristics (pulse time and wavelength)

ICP – MS PerkinElmer « Nexion 300d »
- Sensibility : ~ 5x10^8 hits/ppm
- Background noise : <1 hit mass 220
- Resolution : from 0,2 to 0,7 amu at 10% peak height

Ultrasonic nebulizer CETAC «U-6000AT+»

Coupling LA-ICP/MS used set-up



Y-shaped piece

Laser ablation CETAC « LSX-213 G2 » :
- Pulse length : ~ 5 ns
- Laser wavelength : 213 nm
- Ablation frequency : 1 – 20 Hz
- Maximum energy / shot = 4 mJ
- Ablation diameters= 5 – 200 µm

Experimental design

Factors and responses : Considering several bibliographic sources, influences of **12 factors** of the coupling are monitored on **3 responses** .

Sample : A massive solid of glass matrix called **NIST 612**, is used to identify the influent factors

Experimental design types: Experimental designs of Plackett and Burman (involving the Hadamard matrix) are selected for this study

12 factors ➔ 32 experiments

Variable	Factor	Levels -	Levels +
X_1	Carrier gas flow rate (L/min)	0,5	1
X_2	Nebulisation gas flow rate (L/min)	0,9	1,1
X_3	Repetition rate (Hz)	10	20
X_4	Incident energy of a pulse (%)	25	75
X_5	Crater diameter (µm)	50	150
X_6	ICP power (W)	1250	1500
X_7	Plasma gas flow rate (L/min)	15	18
X_8	Torch depth (mm)	0	0,5
X_9	Integration time per peak : Dwell time (ms)	10	30
X_{10}	Number of scans	10	30
X_{11}	Laser travel speed (µm/s)	25	50
X_{12}	Number of repetitions	1	3

Responses
- Raw intensity in U
- Raw intensity in Zr
- Intensity ratio U/Zr

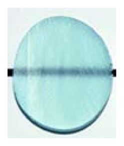
Table of the selected factors

INFLUENCING PARAMETERS

Nebulisation gas flow rate, crater diameter, Incident energy of a pulse, carrier gas flow rate and shot frequency

Influencing parameters optimisation

Approach followed : Semi quantitative analyses based on three different reference materials.



Standard ➔ NIST 612

Samples ➔ NIST 610 and Zircon 91500

Optimised parameters :
Nebulisation gas flow rate= 0.5 L/min **Shot frequency** = 20 Hz
Crater diameter = 100 µm **Carrier gas flow rate**= 0.6 L/min
Incident energy= high for glass matrix and low for zircon matrix

Other influencing parameters found in the literature :
Ablation mode= raster 400 hits/crater **Y-shaped piece angle** = 60°

Use of optimal settings

Method : Direct semi quantitative analysis of the prototypical corium from Cadarache calibrated with **Zircon 91500** and compared to MEB/EDS results.

	Microscopy Analyses	ICP/MS Analyses		Relative error (%)
Uranium (weight %)	35.01	41.80		19
Zirconium (weight %)	20.84	21.55		3
Weight Ratio U/Zr	1.68	1.96		17

Results table including relative errors on U, Zr and U/Zr measures using prototypical corium from Cadarache

Prospects

The continuation of this work consists in applying the optimal settings determined for the prototypical corium from Cadarache to other experimental coriums.
The experimental steps (research, optimisation and use of the influencing parameters) could also be applied to minor elements analyses in corium (Fe, Mg, Al...).

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Référence: Fanny Claverie. Développement et applications d'un système laser femtoseconde infra-rouge basse énergie et haute cadence de tir pour l'analyse d'éléments trace dans les solides par couplage ablation laser / ICPMS. Thèse 01/09 Université de Pau et des Pays de l'Adour