

## Zirconium molybdate hydrate precipitates in spent nuclear fuel reprocessing.

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**Abstract** – This paper presents through 2 posters a general overview studies realised by CEA teams on deposits observed in the La Hague plant dissolution facilities. Their main constituents are metallic debris bound together with zirconium molybdate hydrate. A comprehensive study of zirconium molybdate hydrate formation included nucleation and growth kinetics was developed. Fouling mechanisms were consequently explained as influenced by the operation conditions. Pu insertion was also overviewed. Its behaviour is important when curative and preventive chemical treatments are considered.

### INTRODUCTION

These last years, the formation of solid deposits has been observed in the La Hague plant dissolution facilities. Samples of solids were removed for expertise: molybdenum and zirconium are the two major components of the solid identified as zirconium molybdate hydrate (ZMH), of formula  $ZrMo_2O_7(OH)_2 \cdot 2H_2O$ , as the first chapter shows.

In order to prevent or limit the formation of ZMH in industrial plants, a comprehensive study was undertaken to better understand the fouling mechanisms in which ZMH takes part.

These laboratory studies followed a logical development. At first interaction between molybdenum and zirconium in nitric acid was studied aiming at identifying the precipitation precursor. After measuring the solubility of ZMH, nucleation kinetics were described using the Volmer and Weber theoretical description, leading to a ZMH stability chart in nitric acid near usual operating conditions. The nucleation kinetics were completed with the crystal growth kinetics which, from the stability chart, appears to be the major contributor to fouling.

When ZMH is formed in presence of Ce(IV) or Pu(IV), they are included in the precipitate. Pu or Ce are included probably under the form of a solid-solution thus modifying the final compound as a mixed Pu-Zr molybdate hydrate. The insertion of metallic cations modifies the properties of the solid solution and particularly its solubility which increases and influences fouling.

### COMPOSITION OF SOLID DEPOSITS

Several samples of the solid deposits were removed from different parts of the dissolvers

and received in CEA-Atalante laboratories for characterisation.

These deposits are black powders composed of fuel cladding metallic fragments and precipitate agglomerates. SEM (Scanning Electron Microscopy) showed crystallised aggregates.

Chemical characterisation of the solids was performed by linking several chemical treatments in order to selectively separate the different elements:

1. Washing of the solids in 1N  $HNO_3$  to eliminate the dissolution solution residue,
2. soda treatment to dissolve the molybdenum,
3. boiling nitric acid dissolution of zirconium (as a fission product :  $Zr_{FP}$ ) and plutonium,
4. cladding material ( $Zr_{cladding}$ ) dissolution with a  $HNO_3/HF$  mixture.

The measurement techniques used for chemical characterisation were ICP/AES for Mo, Zr, and some metallic elements, mass spectrometry for U and Pu, and radiometric spectrometries for the main  $\alpha$  and  $\gamma$  radio-emitters.

The chemical characterisation results showed that:

- the main constituent of the solid deposits is Zr cladding from 30 % to 70 % (% of mass),
- the metallic debris are bound with a variety of ZMH with atomic ratio  $Mo/Zr_{FP}$  varying from 2.1 to 4.0 (above the stoichiometric value),
- the solid materials also contain Pu with varying fractions from 0.3 to 1.2 % in mass, mainly trapped with the ZMH precipitate,

- low amounts of U were detected (from 0.2 to 1.7 %), most probably originating from the dissolution solution impregnation.

The  $\alpha$  activities for these materials vary from  $3.6 \cdot 10^1$  to  $1.9 \cdot 10^2$  MBq per gram of solid deposit, with more than 90 % of the  $\alpha$  emitters recovered in the nitric acid dissolution step.

The  $\gamma$  emission represents  $10^3$  to  $6.3 \cdot 10^3$  MBq per gram of solid deposit, with the major  $\gamma$  emitter  $^{125}\text{Sb}$ , both fission and activation product.  $^{106}\text{Ru}$ ,  $^{106}\text{Rh}$ ,  $^{60}\text{Co}$ ,  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$  are also present.

#### SOLUBILITY AND SPECIATION

At first, the molybdenum(VI) chemistry in highly acidic media (0.5-3 M perchloric acid) at 25°C was investigated by UV absorbance spectrophotometry [1]. The experimental results obtained were interpreted by mathematical analysis methods. They provided information on the chemistry of Mo(VI) solutions in the absence of complexing agents [2].

Molybdenum(VI)-zirconium(IV) chemistry was studied by UV spectrophotometry in the same acidic media [3], revealing the existence of a complex between the two species. Within the experimental domain ( $2 \text{ M} \leq [\text{HClO}_4] \leq 3 \text{ M}$ ,  $[\text{Mo(VI)}] < 10^{-2} \text{ M}$ ,  $[\text{Zr(IV)}] < 10^{-2} \text{ M}$ ) a complex with 1:1 stoichiometry is formed with a conditional constant of approximately 200 at 25°C.

The study of ZMH solubility was investigated in nitric acid media showing no significant effect of temperature from 60 to 90°C. Solubility increases with nitric acid concentration as an empirical law:

$$s = 6 \cdot 10^{-5} \cdot [\text{HNO}_3]^{1.85} \text{ (mol.L}^{-1}\text{) for } 1 < [\text{HNO}_3] < 3 \text{ M}$$

#### NUCLEATION PHENOMENA

As shown above, ZMH intervenes in the fouling mechanism as the equivalent of a binder in cement: insoluble particles of debris are bound together by ZMH crystals or crystal agglomerates. However, before this study, it was unclear why ZMH was present in the first place, and how fouling proceeds continually. Several processes lead to fouling but the main process of interest here comprise:

- A precursor step leading to an initial deposit, by either particle deposit or surface nucleation. This last event being promoted either by a local supersaturation (heating for example), or/and catalyzed by the surface,
- formation by crystal growth and/or particle deposit of debris and ZMH

particles, depending on the solidity of the deposit.

Knowledge of the stability of solutions towards ZMH precipitation are therefore of prime importance. Not only will it determine the precursor step, but for example the existence or not of free particles that could lead to radically different types of fouling. Operating conditions can then be modified in consequence.

#### Background

The classical theory of nucleation as exposed by Volmer and Weber [4], expresses the rate of primary nucleation as follows:

$$R_N = A_N \exp\left(-\frac{B_N}{(\ln S)^2}\right) \quad (1)$$

Where  $R_N$  represents the number of nuclei formed per unit volume and time thus  $R_N$  is the inverse of the induction period,  $t_{ind}$ .  $A_N$  and  $B_N$  are kinetic parameters.  $S$  is the supersaturation ratio which represents the chemical driving force.

Although supersaturated solutions are always unstable, substantial precipitation can occur only after relatively long periods of time, thus the appellation “metastable state”. The boundary between a metastable state and an unstable state is a function of the observation time scale chosen. As can be shown by equation (1), for a given observation time scale, a critical supersaturation can be determined above which nucleation appears to be spontaneous. Such critical supersaturations can be achieved by concentration variations, temperature variations, solubility changes or by extending solution residence times in through flow experiments (in relation to the observation time scale).

Here they are obtained by plotting experimental induction periods versus solution supersaturation ratios. A double jacket well stirred reactor was specially designed for induction period measurements, and was validated on several runs by correlating with regular solution sampling. The solids produced were systematically sampled and analyzed by SEM, X-ray diffraction and thermal analysis. Throughout the whole study only ZMH was found, showing always the same crystal habit as cubic particles.

#### Nucleation Kinetics Results

The identical crystal habit allows interpretation of induction times as Fig. 2., showing a good linear fit with no breakage over the range of supersaturations experimented : nucleation is of only one type, most probably heterogeneous and relation (1) holds. The critical supersaturations are resumed on a stability chart for acidities

between 1.5 and 3 N. Hence the stability of the supersaturated solutions can be predicted using the concentrations and the solubility of the end product, whatever the acidity within the experimental range.

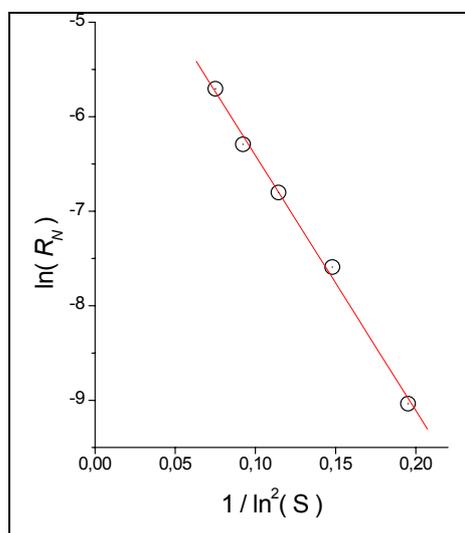


Fig. 1: nucleation rates as relation (1), for 1.5 N at 80 °C.

Fig.2 shows that industrial liquids, in the dissolver for example, are usually below, but close, to the critical supersaturation concentrations. This means that nucleation probably does not occur freely in the solution, but by the occasional crossing of the frontier either by a process increasing the concentrations (A on Fig. 3), for example by solvent evaporation on all surfaces that are periodically immersed, or hot spots (B). Another, cause being residence times much higher than the usual few hours or stagnant zones, corresponding to the observation time scale chosen here.

Thus, fouling at least at the bottom of the dissolver, is most probably initiated by limited particle deposit and surface nucleation, especially on hot spots. The main growth mechanism is crystal growth on the existing deposit (scaling) and nucleation on the accumulated debris. Continuous precipitation is not a contributor to fouling.

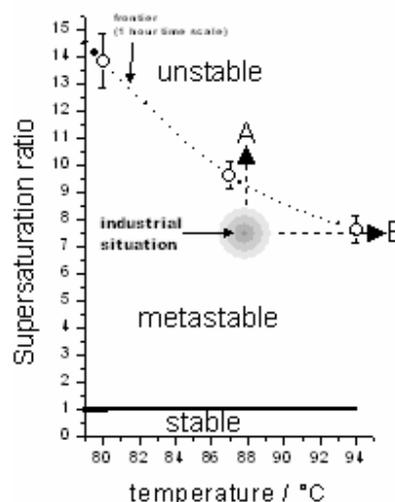


Fig. 2: stability chart of ZMH in nitric acid.

### CRYSTAL GROWTH AND SCALING

The previous chapter pointed out the importance of crystal growth. It is therefore of interest to know how different operating conditions can limit this phenomena.

The results obtained above gave the condition suitable for hot spot surface nucleation. Thus, ZMH particles were nucleated on the metallic surface of a Quartz Crystal Balance completely covering the surface. Thus it was possible to measure relative average growth rates over all the crystals and crystal surfaces present keeping at the same time the concentrations in solution close to constant.

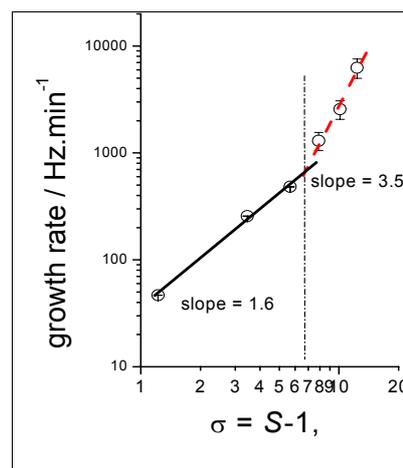


Fig. 3. Crystal growth rates

### Growth Kinetics Results

A typical plot of the mass increase rates (in Hertz per minute) is shown in Fig. 3 for nitric acid 3 N

at 80 °C. It is shown that for small supersaturations,  $g$  is equal to 1.6, meaning probable growth limiting mechanisms to be combined volumic diffusion, adsorption and surface diffusion [5]. Above  $S=8$ ,  $g$  is near to 3.5. Although the solution is far from critical supersaturation, this clearly indicates growth by surface nucleation by the creation of new kinks or new crystallites. This is the probable industrial situation: enhanced scaling obeying a high power law.

#### PU INSERTION

One of the characteristics of ZMH is the potential to intake cations such as Te(VI), Ce(IV) or Pu(IV). An experimental study was undertaken in order to explain how such ions are entrapped.

Firstly it was observed that when ZMH is synthesized near industrial conditions and in the presence of Ce(IV) or Pu(IV) in the nitric solution, its progressive dissolution in nitric acid systematically leads to constant Zr, Mo and Ce(IV) or Pu(IV) concentrations. Adsorption and entrapment of the liquid solution in an eventual closed porosity was ruled out. Moreover, it was shown that Ce(IV) and Pu(IV) had relatively close behaviours. All further studies were therefore carried out on Ce(IV), and checked on a few points with Pu(IV).

Firstly, X-Ray diffraction and microprobe analysis confirmed that when ZMH was synthesized near industrial conditions the Mo/Zr ratio was systematically above 2 (2.2), Mo and Zr being always at oxidation states of VI and IV within the solid.

Secondly, further studies on mixed zirconium-cerium molybdate hydrates showed a probable insertion of cerium into cationic vacancies for low Ce concentrations and the substitution of Zr by Ce for higher concentrations by respecting Vegard's lattice deformation law, thus most probably forming a solid solution.

#### LIQUID SOLUTION - SOLID SOLUTION EQUILIBRIA

The insertion of plutonium forming mixed plutonium ZMH (ZPMH) affects greatly the solubility and therefore the supersaturation ratios of industrial solutions. In its turn, the solution composition affects the plutonium content of ZPMH. In order to use all the precipitation and growth data on ZMH, and, above all, explain and predict the plutonium content, a theory describing liquid solution and solid solution interactions was applied [6]. Such a description as formulated by Lippmann was used with

success at least at low content ZPMH. Pu content is now predicted.

#### ZPMH SOLUBILISATION STUDIES

Mechanical action and chemical action are foreseen to remove the deposits. Chemical action can be seen as two different strategies: preventive and curative treatments. However, the presence of Pu in the ZPMH solids means keeping Pu in a soluble form all the way from the dissolution step down to the reagents' destruction, therefore limiting the choice.

Preventive treatment requires only a low dissolving power chemical, easily used and destroyed.  $H_2O_2$  has therefore been proposed and tested on real deposits. Small solubilities of circa 3g/L of ZMH were obtained, but probably sufficient for preventive treatment, were measured.  $H_2O_2$  destruction, probably by degassing or contact with radio-emitters, is a limiting factor.

Curative treatment requires a high power chemical, forming strong soluble Pu complexes. Carbonate anion ensures high solubilities of at least 90 g/L of ZMH at 1M, and ensures the stability of Pu complexes. Destruction is operated by introducing the solution into nitric acid.

#### FUTURE PROSPECTS

On the one hand, new samplings of solids in dissolution workshop were realised to get further data on deposits and to study optimized dissolution process. This work is currently in progress.

On the other hand, laboratory studies will focus on the synthesis of ZPMH and ZMCH solid compounds of different content in order to fulfill the lay-out of the Lippmann diagram for both systems. Also, special interest will be taken in further studies of the interaction between metallic cations and their speciation in nitric acid solutions.

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