Modelling and simulation of molybdenum extraction by HDEHP ion-exchanger and DMDOHEMA solvating extractant

V Vanel, C Marie, M T Duchesne, X Hérès, V Pacary, L Berthon, D Rudloff, M Bertrand, S. Watanabe

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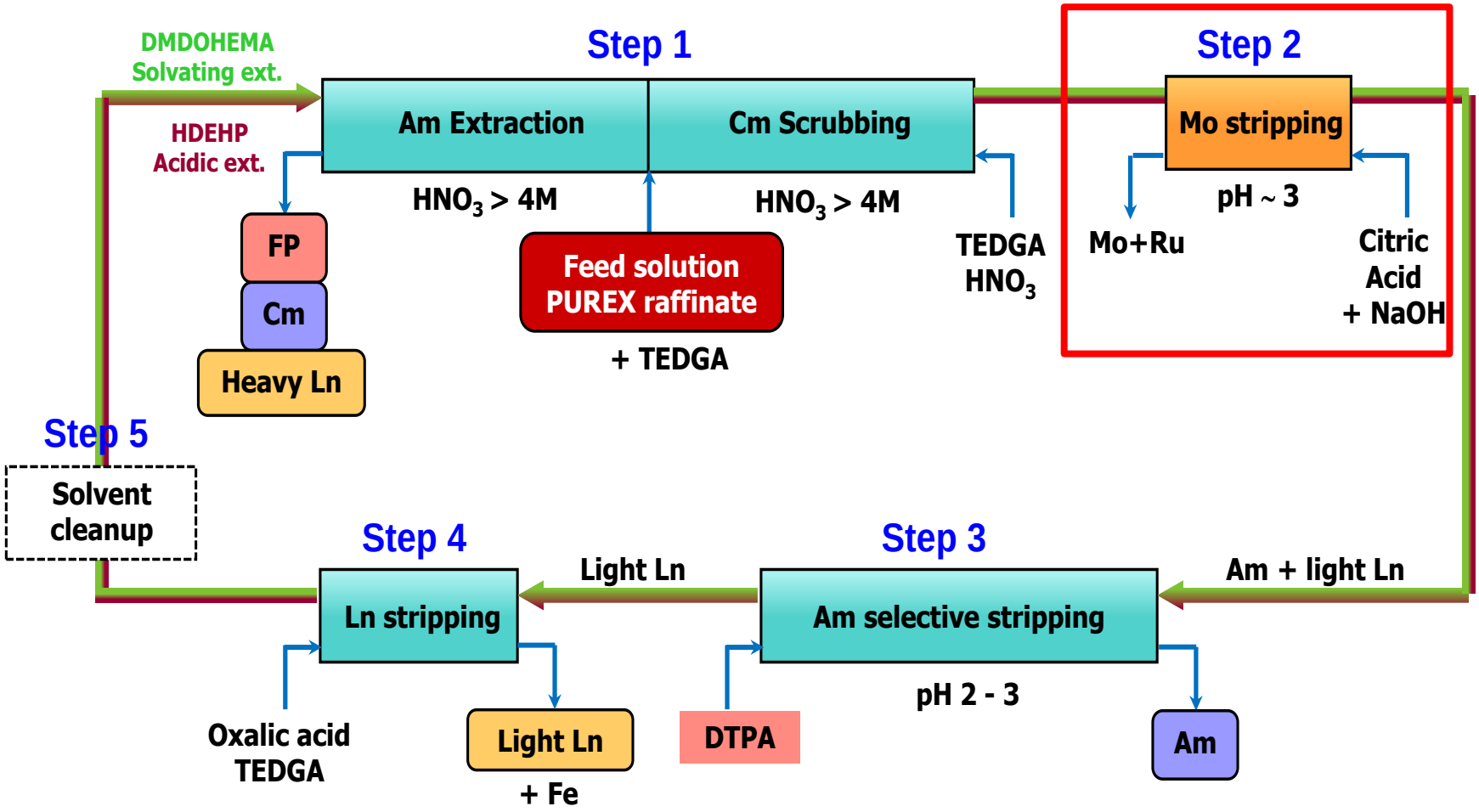
ISEC 2014 – Nuclear Chemistry For Sustainable Fuel Cycles | V. Vanel, C. Marie, M. T. Duchesne, X. Hérès, V. Pacary, L. Berthon, D. Rudloff, M. Bertrand, S. Watanabe

Monday, September 8th, 2014

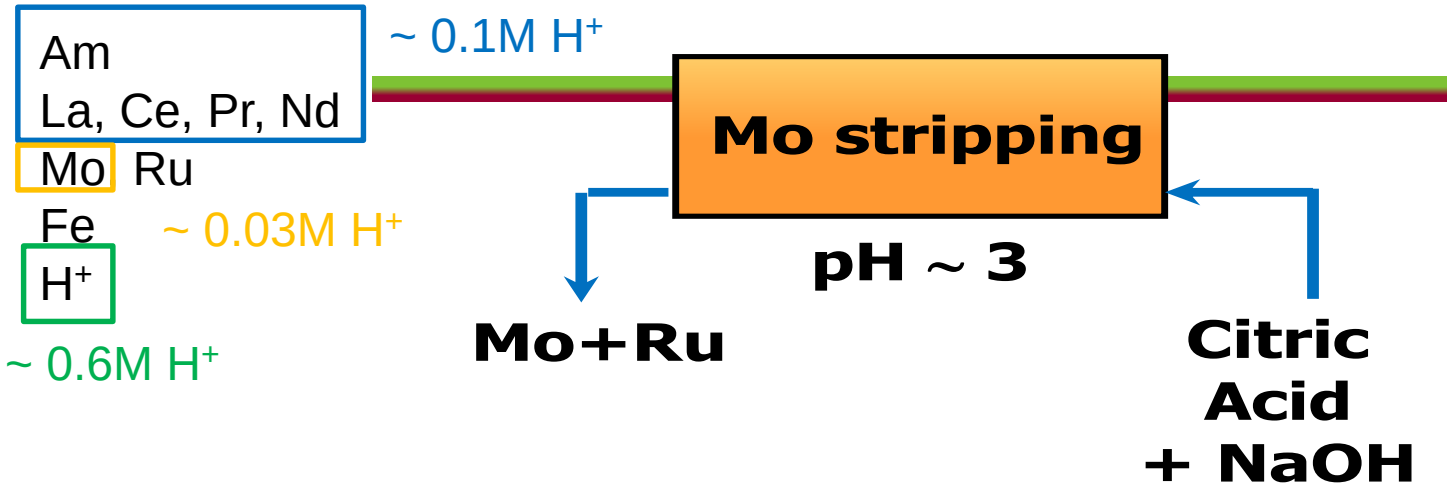
Contents

The EXAm process and the Mo stripping step

- The EXAm process aims at recovering americium alone from the PUREX raffinate



How does the Mo stripping step work?



Change from an acidic medium (4 – 5 M) to weak acidic conditions (pH 2 – 3)
Neutralization of extracted acid by NaOH

Recombination of extracted complexes in the organic phase
4 – 5 M: predominant effect of DMDOHEMA (solvating extractant)
pH 2 – 3: predominant effect of HDEHP (cationic exchanger) => release of H^+

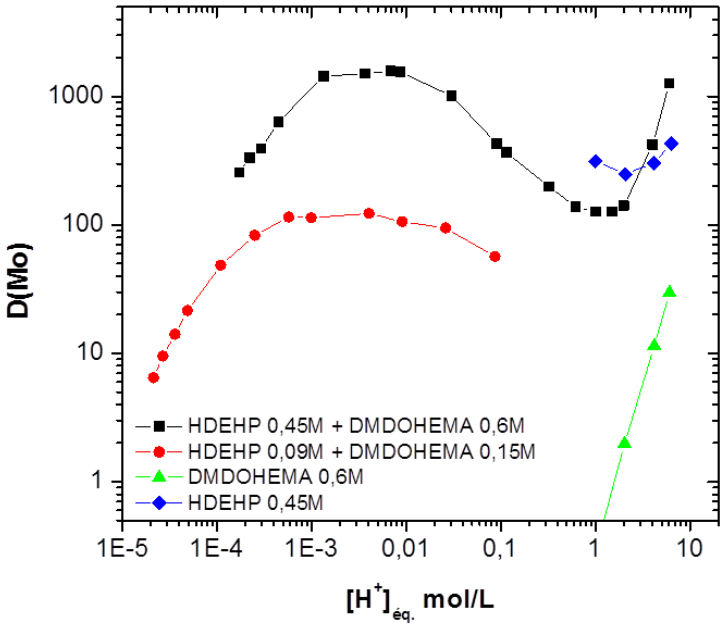
Citric acid: complexing power vs. acid buffer

Stripping of Mo

Approach adopted to build the model

- Determination of constants on batch experiments

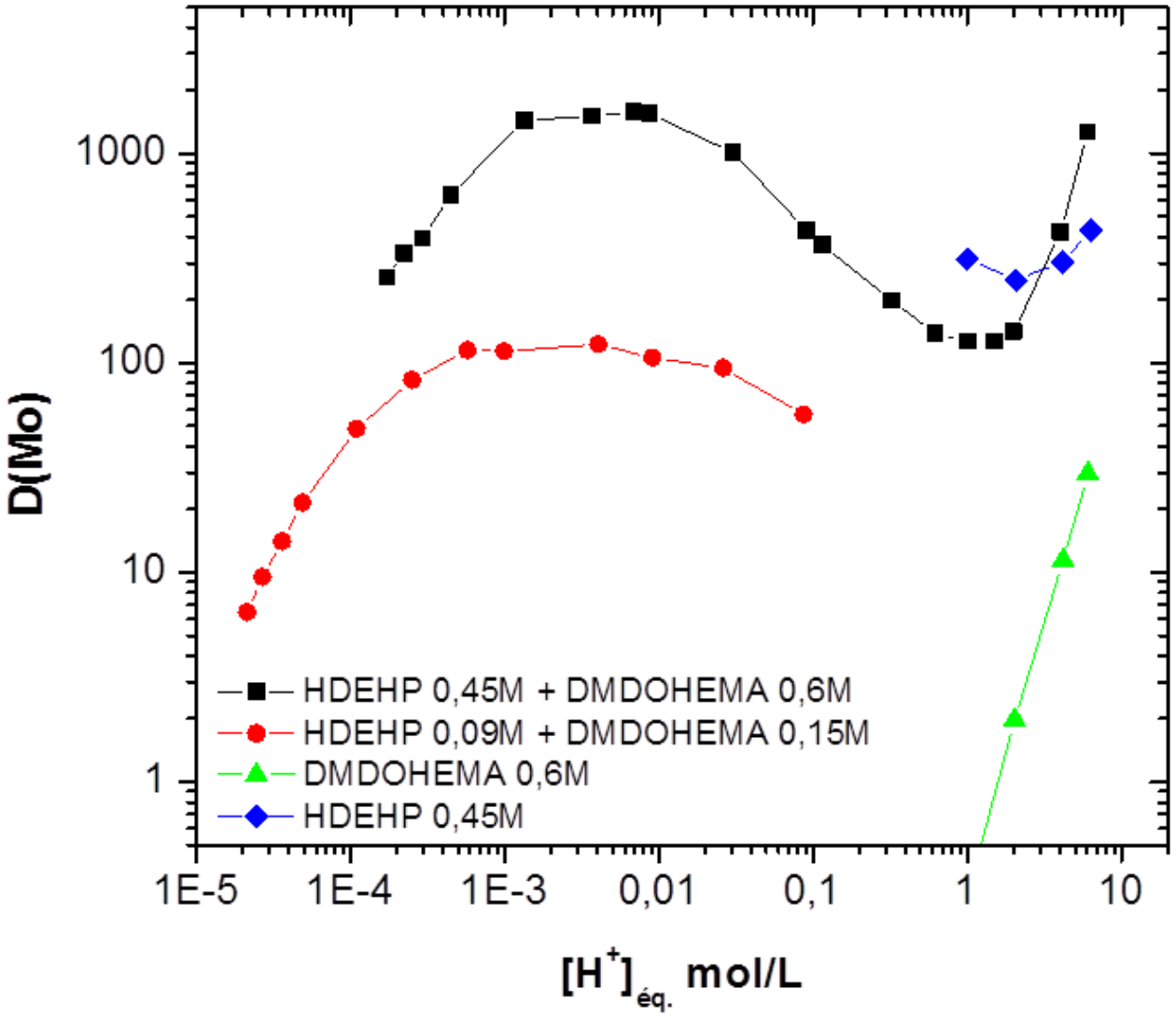
Reference : Marie C., Watanabe S., Vanel V., Duchesne M.-T., Zorz N., Berthon L. Behaviour of Molybdenum (VI) and Iron(III) in {HDEHP-DMDOHEMA-nitric acid} liquid-liquid extraction systems. Paper in preparation



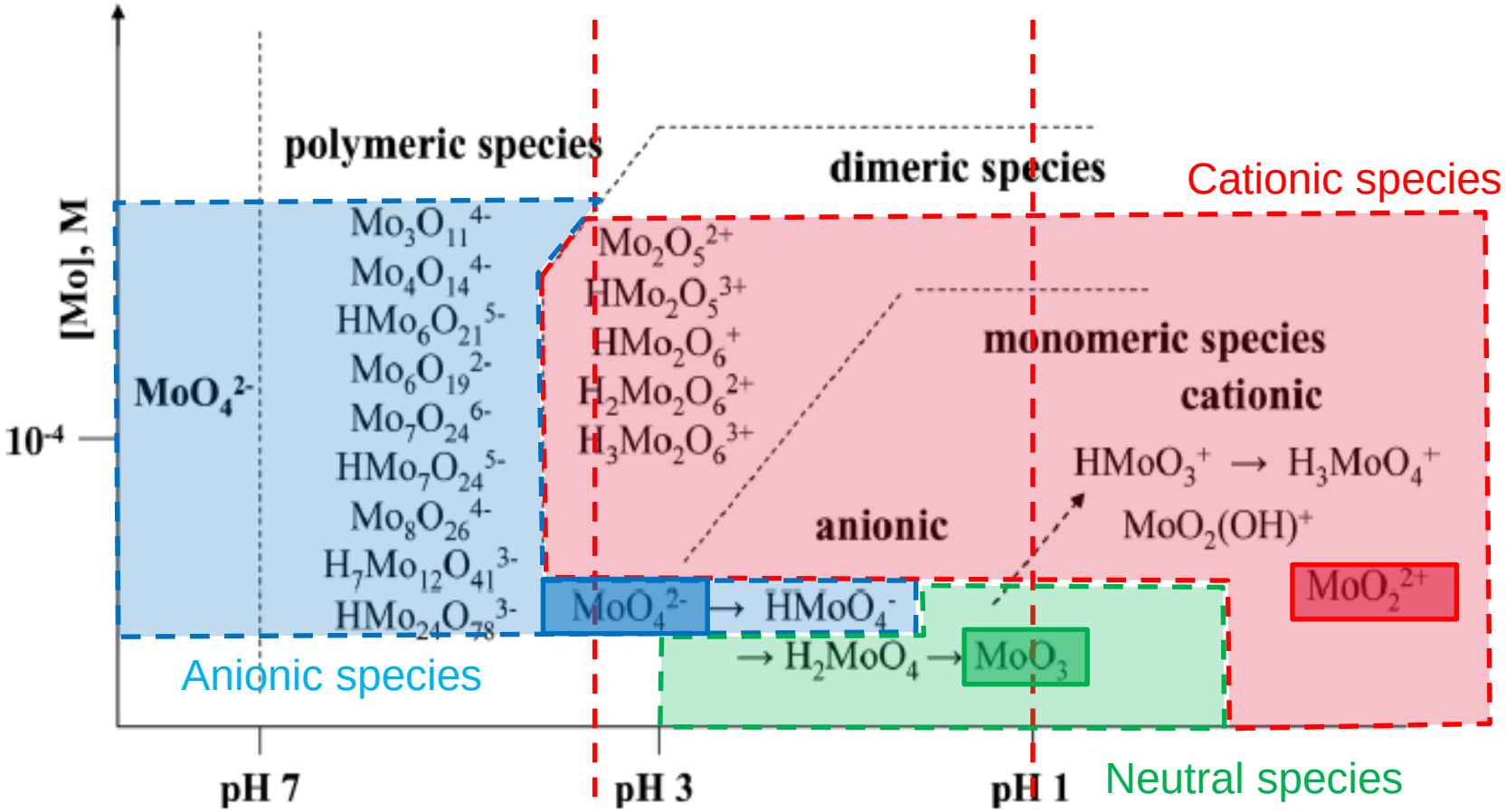
- First validation of the model on a cold test (G1 facility at Marcoule)

Reference : ???

Modelling of Mo(VI) behavior

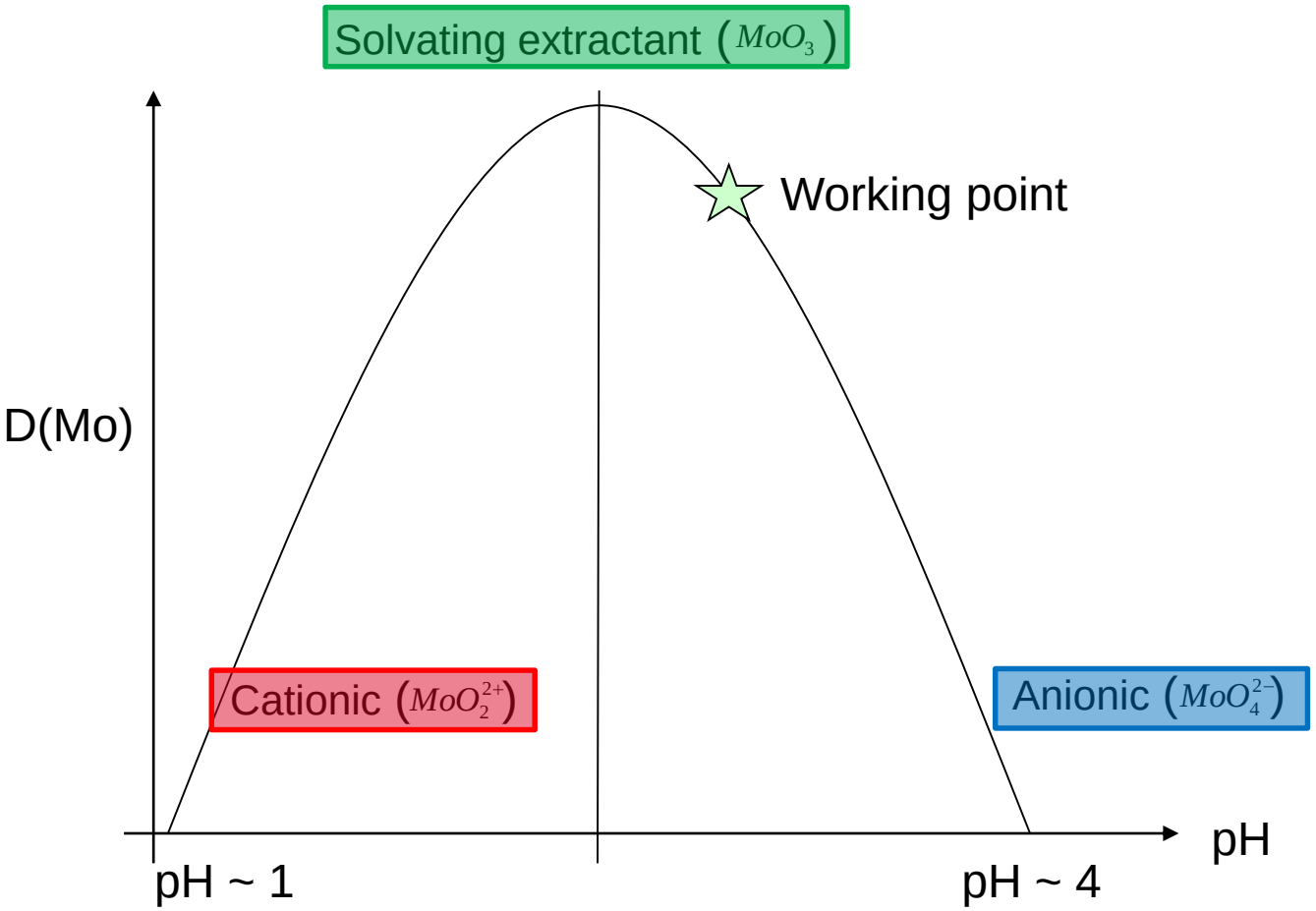


Modelling of Mo(VI) behavior



Ref : Tkac P., Paulenova A. Speciation of molybdenum(VI) in aqueous and organic phases of selected extracting systems, Separation Science and Technology, Vol. 43, p. 2641 – 2657, 08/2008.

Modelling of Mo(VI) behavior

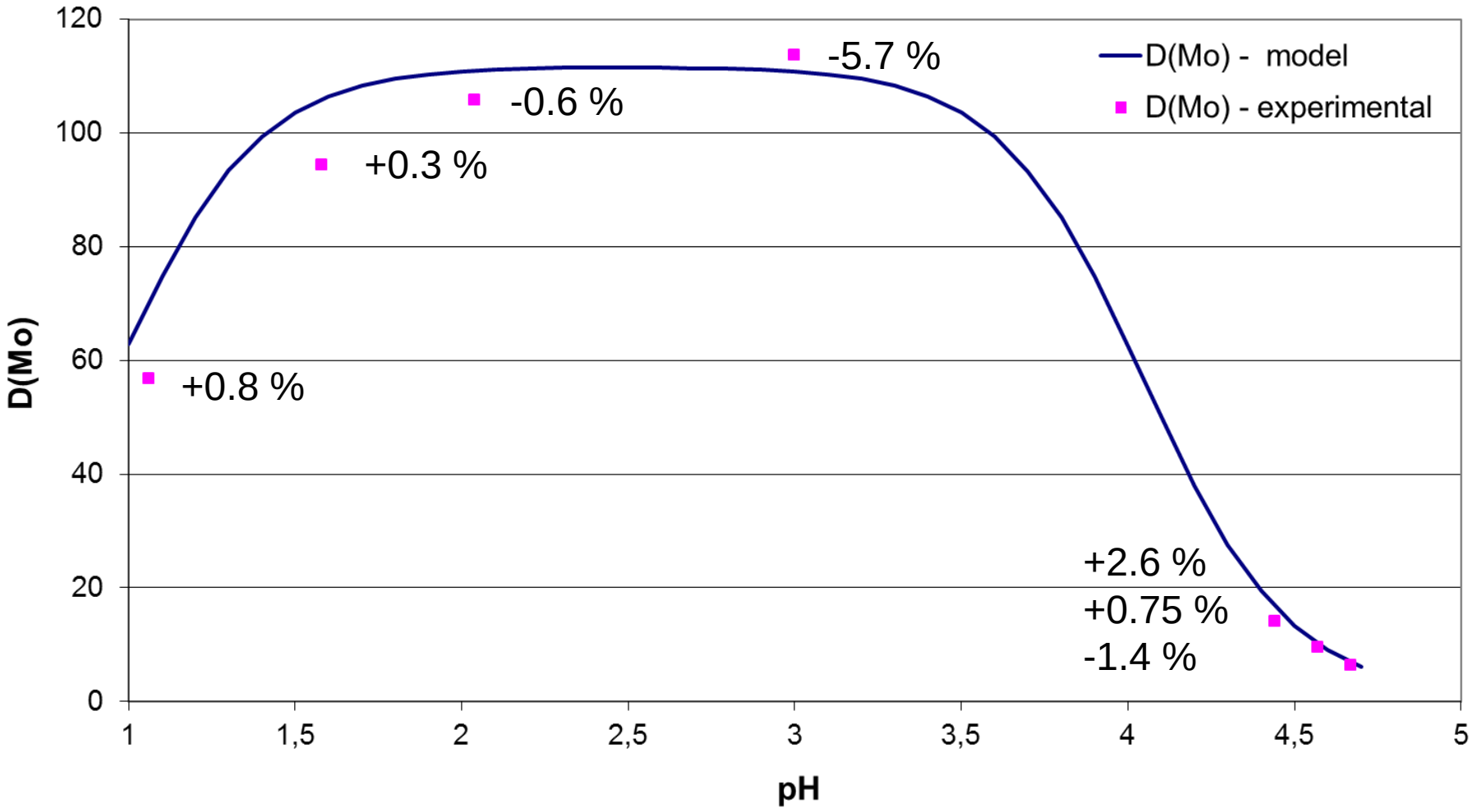


Ref : étude d'un procédé de valorisation du molybdène par extraction par solvant organosphosphore, C. Brassier, thèse CEA-R-5689, 1995

Modelling of Mo(VI) behavior

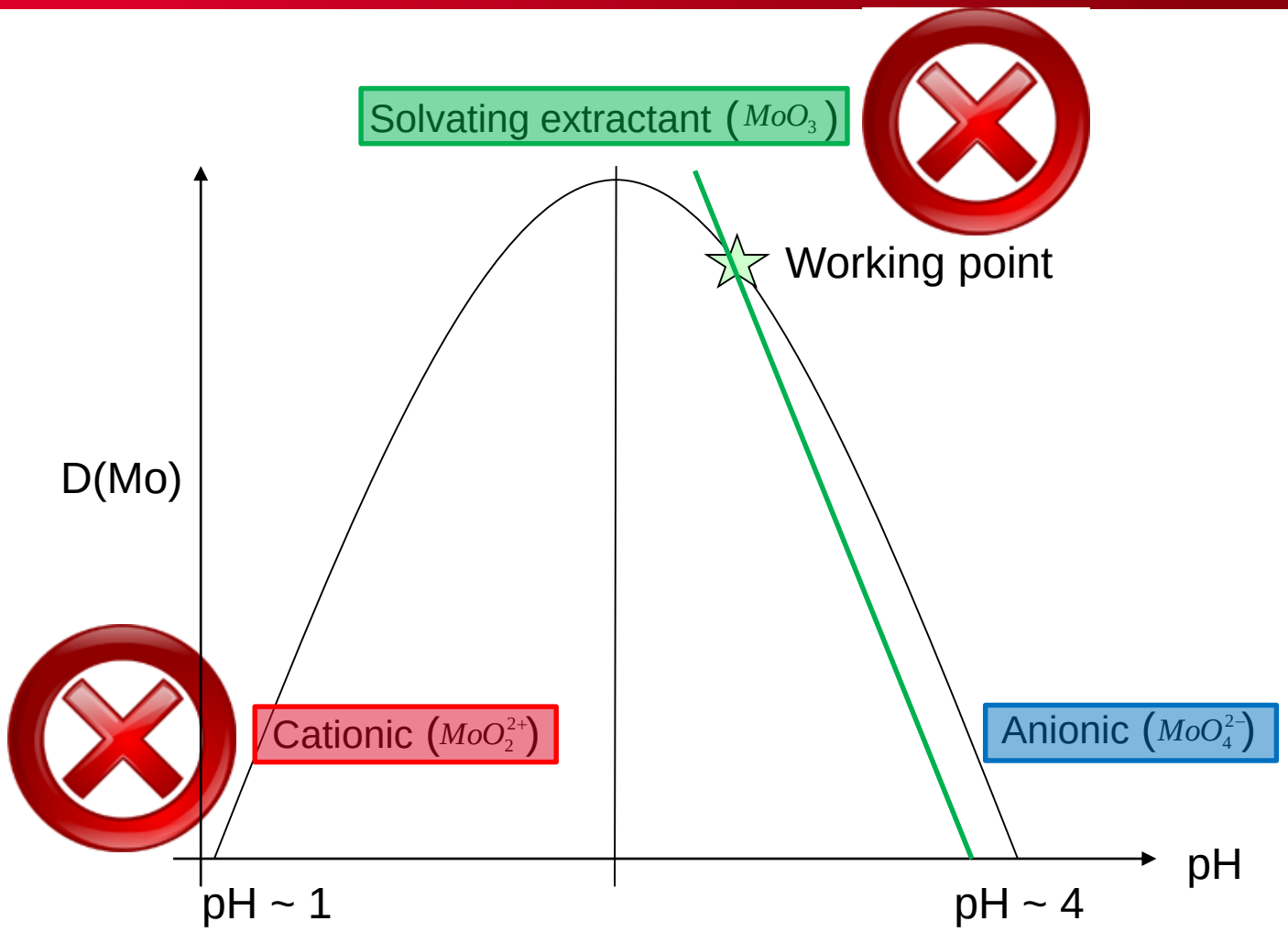
Chemical reaction	Formula	Log(K)
MoO_2^{2+} / MoO_3	$[MoO_2^{2+}] = K(MoO_2^{2+} / MoO_3) \times [MoO_3] \times [H^+]^2$	1.9
MoO_3 / MoO_4^{2-}	$[MoO_3] = K(MoO_3 / MoO_4^{2-}) \times [MoO_4^{2-}] \times [H^+]^2$	8.1
Cation exchanger	$[\overline{MoO_2DEHP_2HDEHP_2}] = K_{ec} \dfrac{[MoO_2^{2+}] \times [\overline{HDEHP}]^4}{[H^+]^2}$ 	4.7
Solvating extractant	$[\overline{MoO_3HDEHP_4}] = K_{es} \times [MoO_3] \times [\overline{HDEHP}]^4$ 	5.5
Anion exchanger	$[\overline{MoO_2DEHP_2HDEHP_2}] = K_{a} \times [MoO_4^{2-}] \times [\overline{HDEHP}]^4 \times [H^+]^2$ 	13.6

Modelling of Mo(VI) behavior

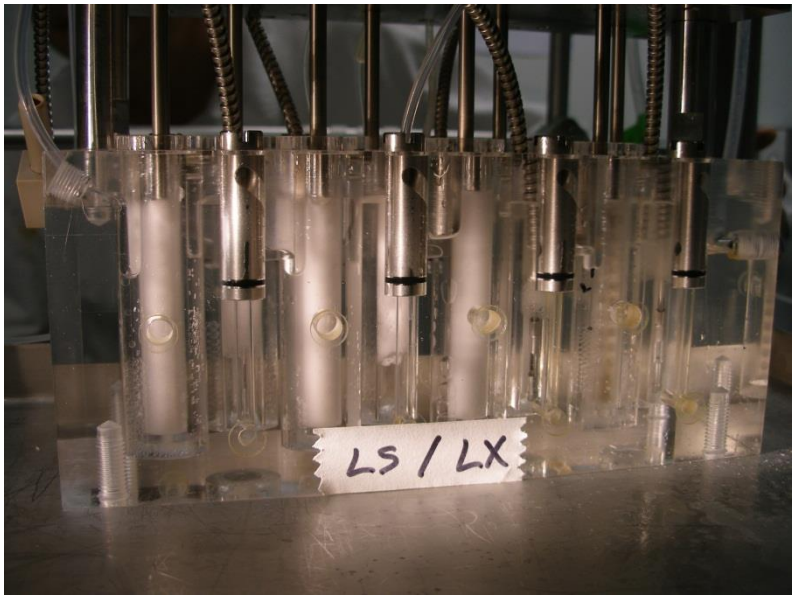


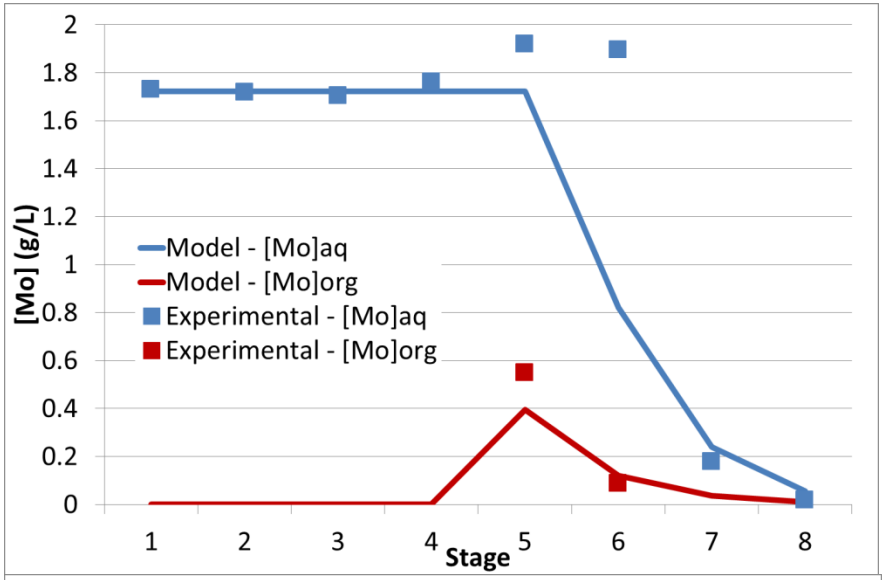
Model seems to be representative of Mo behavior

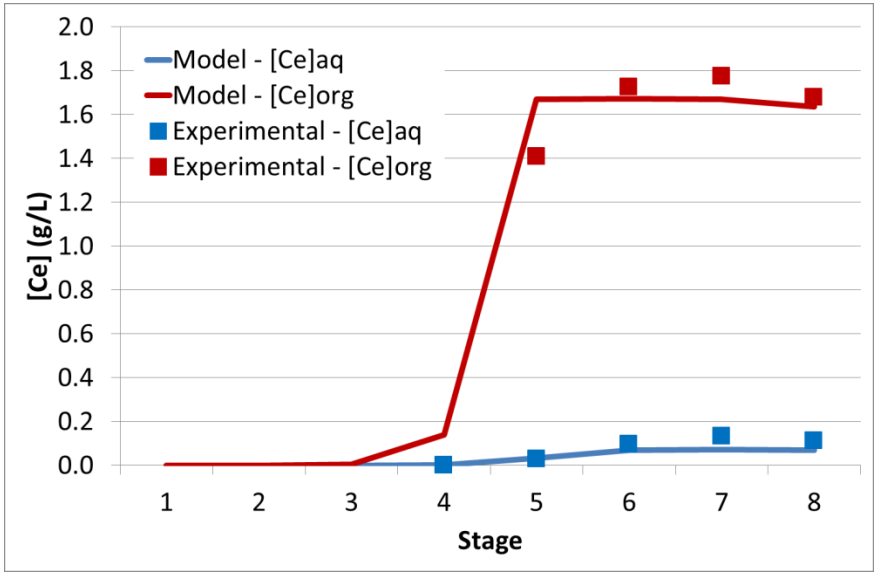
Implementation in the PAREX code

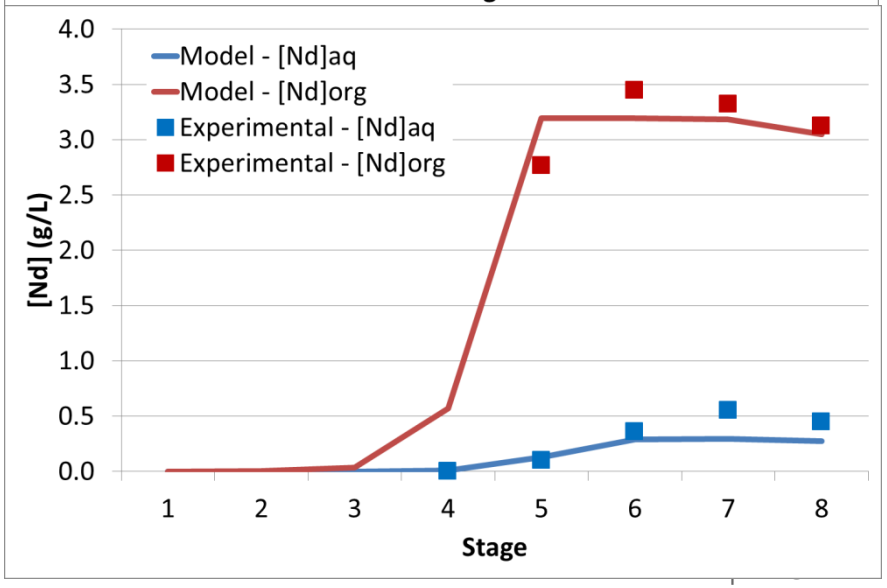


Cold test (G1 facility, Marcoule)

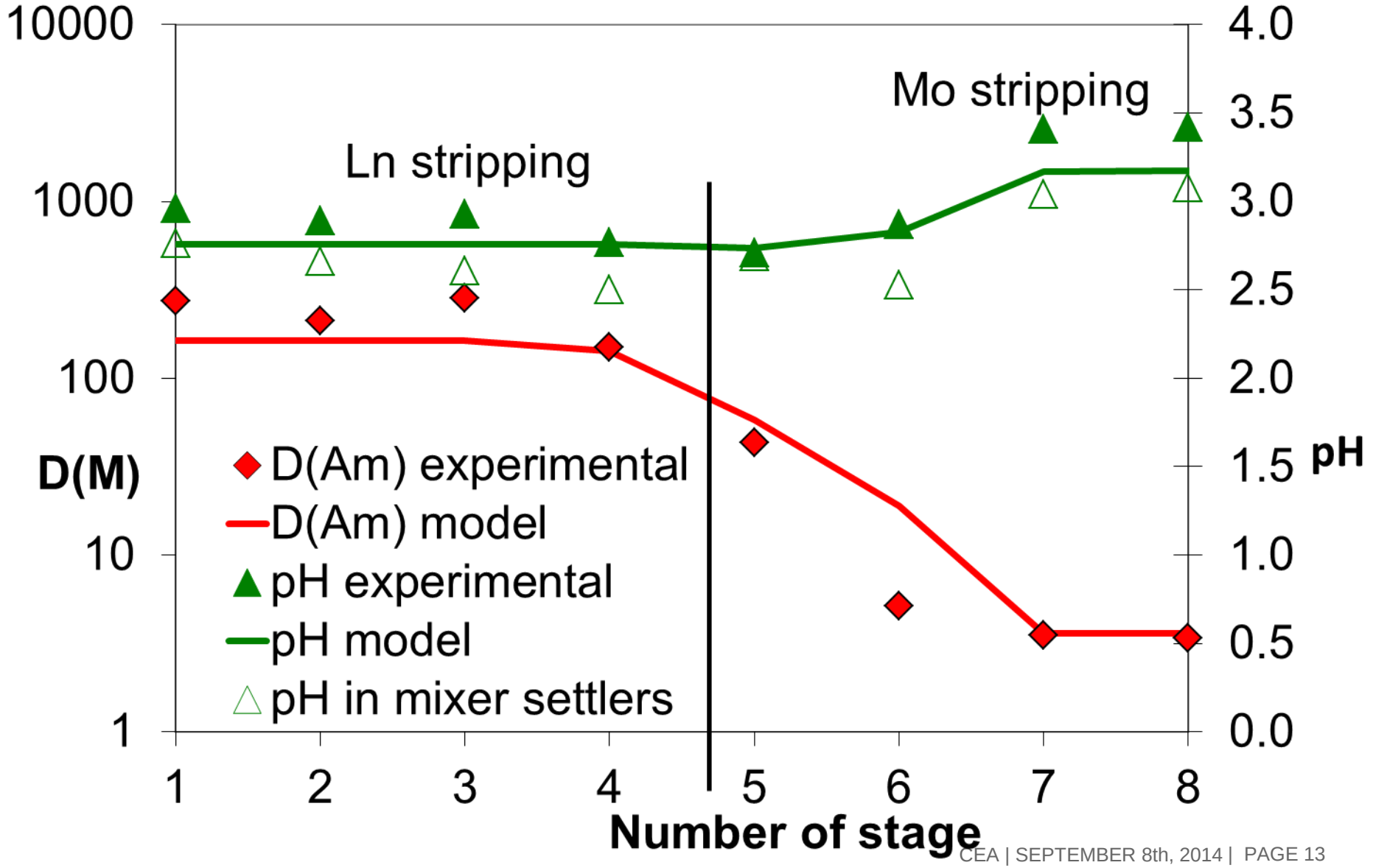








Cold test (G1 facility, Marcoule): trace amounts of Am



Conclusions - prospects

- Conclusions :
  - Modelling quite representative for Am, La, Ce, Pr, Nd and Mo in weak acidic conditions
  - Use of models to propose flowsheets for hot tests, both in trace and macroscopic amounts of actinides.

- Prospects :
  - Implement the complete model in the PAREX code
  - Compare the model to future hot tests (trace and macroscopic amounts of actinides)

Thank you for your attention!

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