

Active dissolution of a silicon-rich austenitic stainless steel in nitric acidic investigated through atomic emission spectroelectrochemistry

B. Laurent, K. Ogle, N. Gruet, B. Gwinner, F. Miserque, M. Tabarant

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DE LA RECHERCHE À L'INDUSTRIE

cea den

ACTIVE DISSOLUTION OF A SILICON-RICH AUSTENITIC STAINLESS STEEL IN NITRIC ACIDIC INVESTIGATED THROUGH ATOMIC EMISSION SPECTROELECTROCHEMISTRY

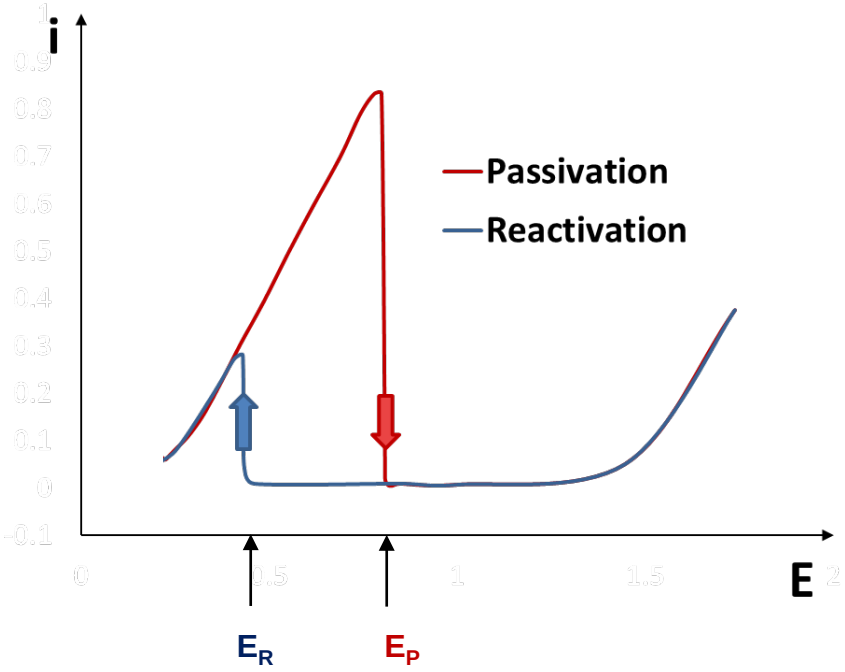
B. Laurent
K. Ogle *(Ecole Nationale Supérieure de Chimie Paris)*
N. Gruet, B. Gwinner *(CEA Saclay)*
F. Miserque, M. Tabarant *(CEA Saclay)*

EUROCORR2016 | Montpellier (France)

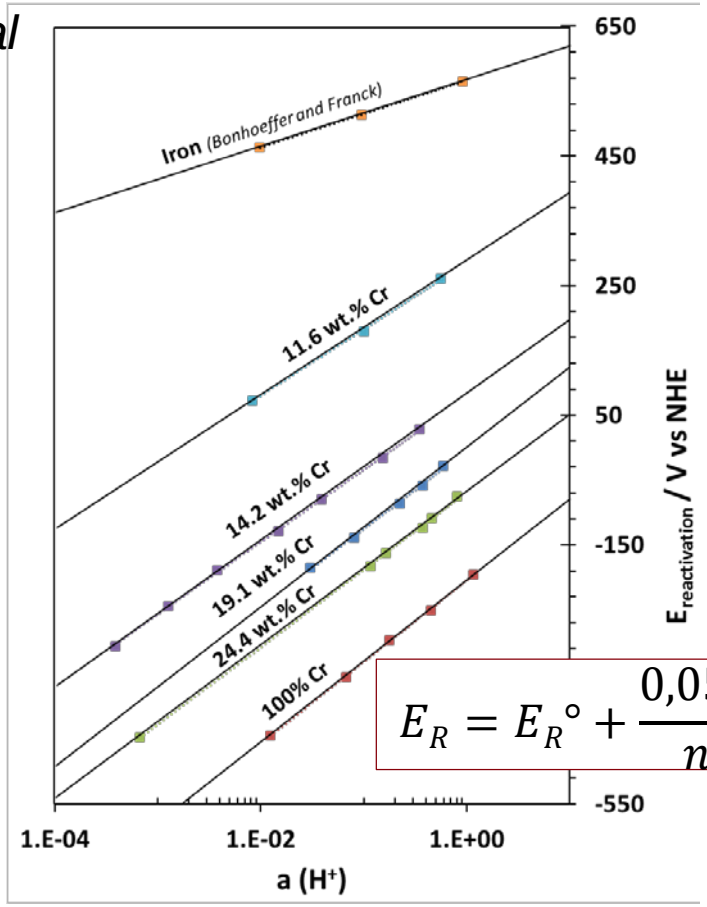
11-15 SEPTEMBER 2016

In situ characterization of a passive film…

…using the reactivation potential



*E_R and E_P of pure iron in **sulfuric acid*** [1]



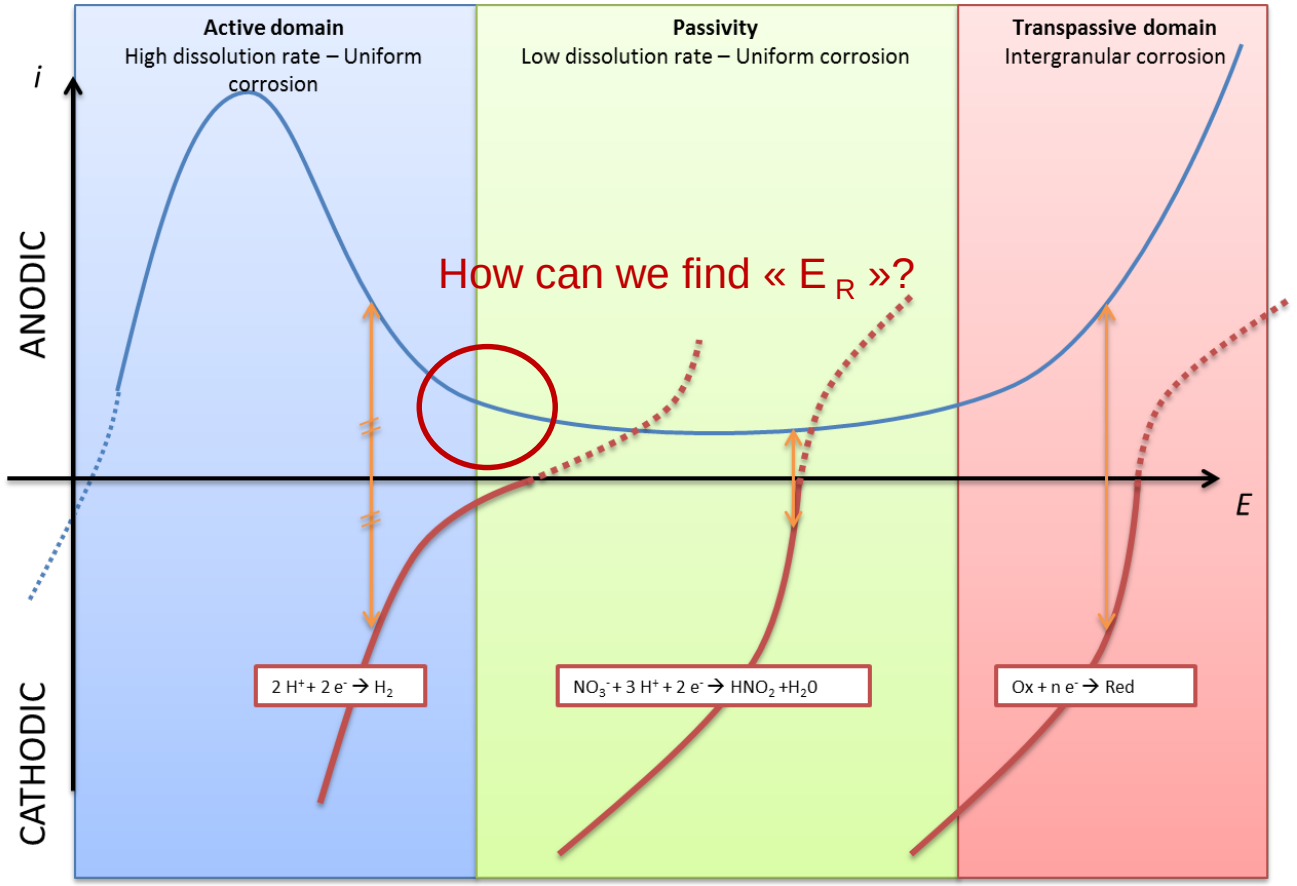
$$E_R = E_R^\circ + \frac{0{,}058}{n} \log a_{H^+}$$

*Reactivation potential **E_R** of various Cr-Fe alloys in **sulfuric acid*** [2]

[1] (Reproduction) Lorbeer, P. and W. J. Lorenz (1981) Corrosion Science **21**(1): 79-86.
[2] (Reproduction) Rocha H-J. and Lennartz G. (1955). Archiv für den Eisenhüttenwesen **117**(933).

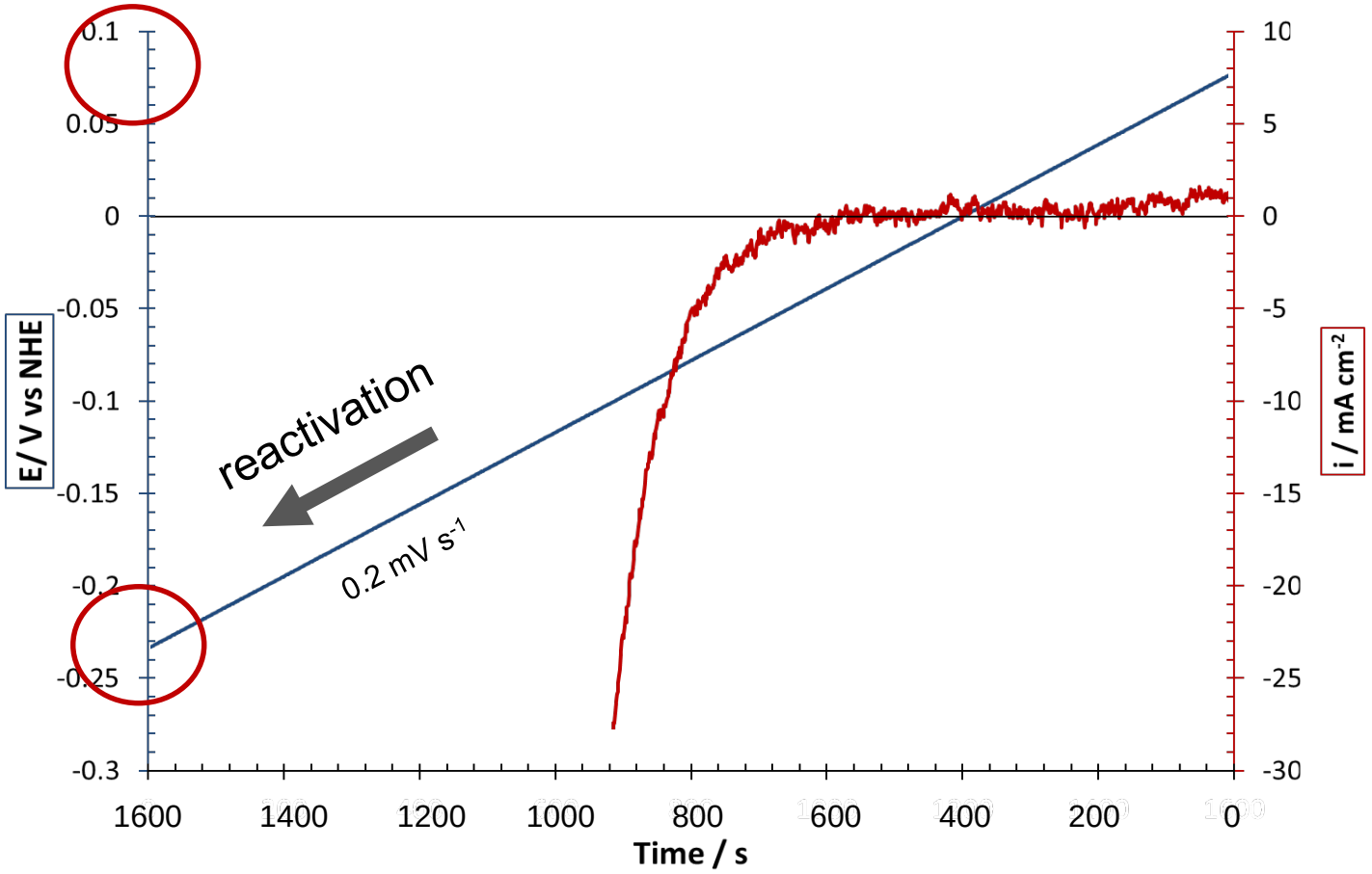
CONTEXT

… of an austenitic stainless steel, directly in nitric acid



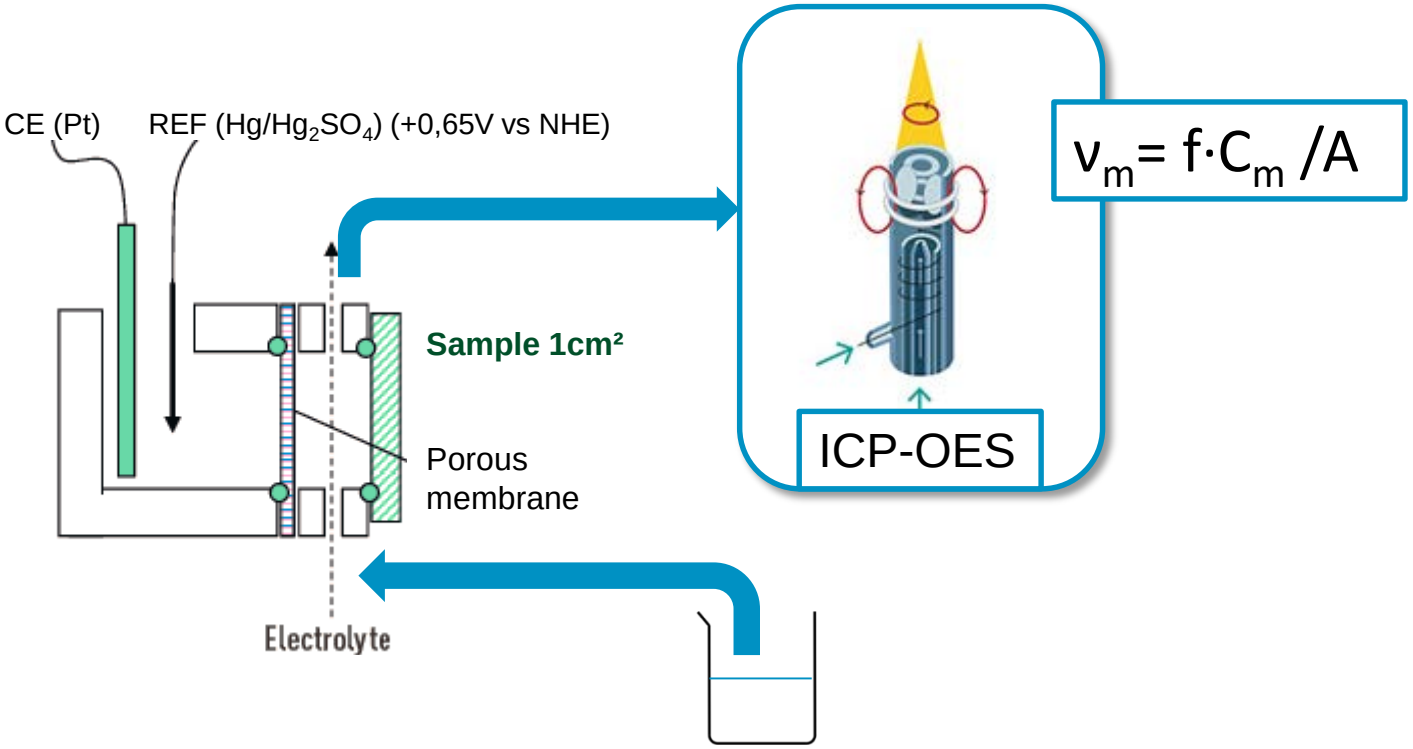
METHOD

Silicon-rich stainless steel – HNO_3 4M – 28°C



Atomic Emission Spectro Electrochemistry

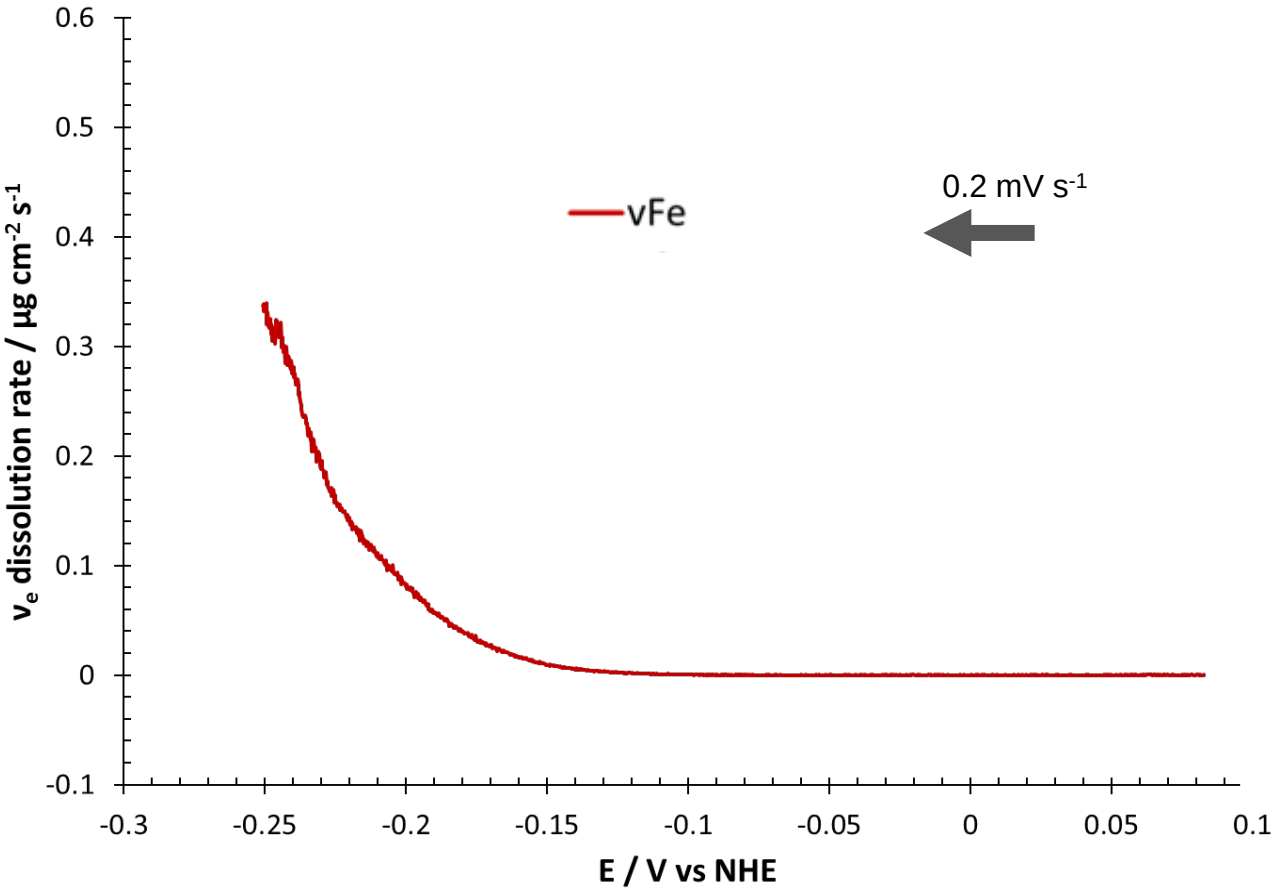
Active dissolution beneath cathodic RR



- f : flow rate (2,8mL/min)
  C_m : concentration
  v_m : dissolution rate
  A : sample's area ($1cm^2$)

REACTIVATION OF THE STEEL

Silicon-rich stainless steel – HNO_3 4M – 28°C

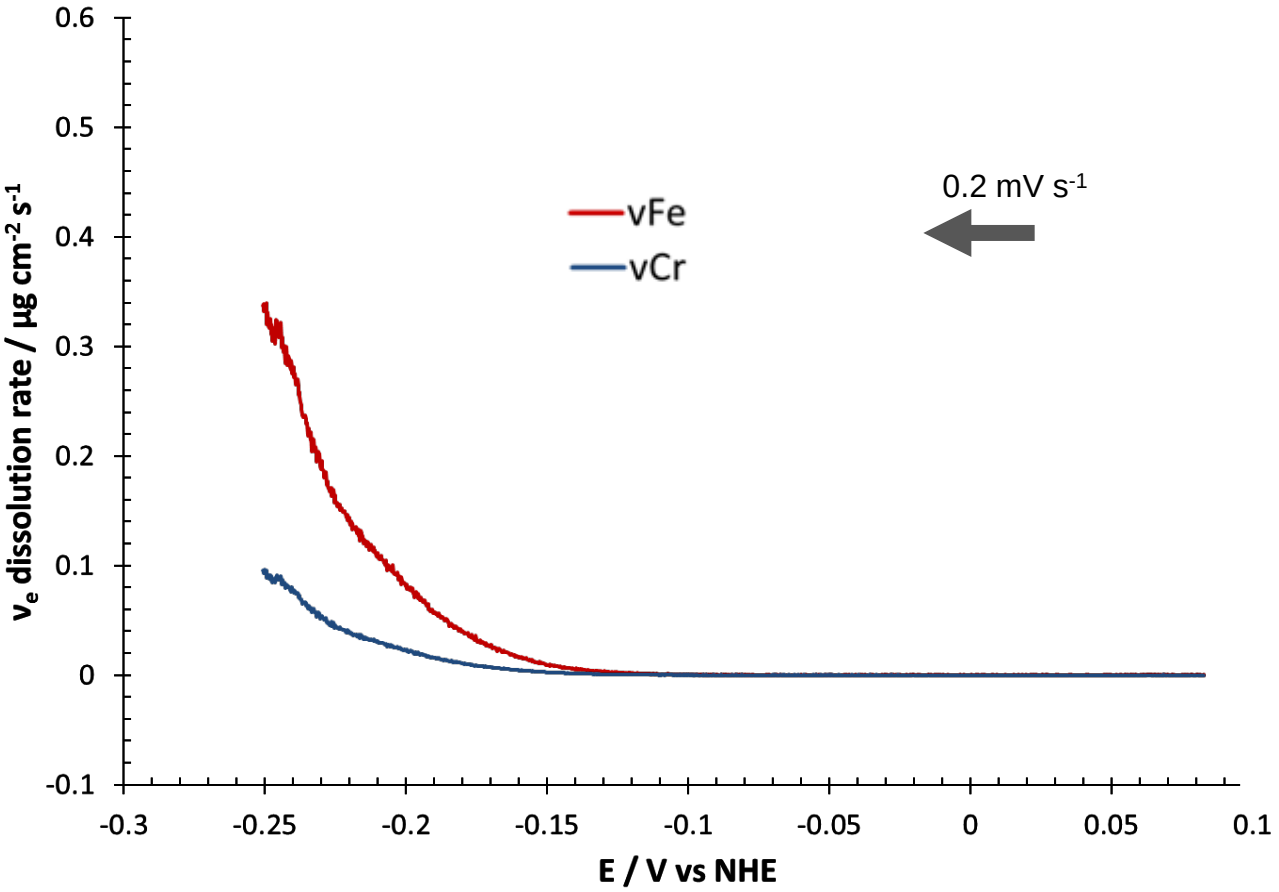


Si-rich SS	Fe	Cr	Ni	Si	C	Mn
%m[1]	59.76	18.79	15.08	3.54	0.029	1.97

[1] Glowing discharge spectroscopy – 150µm – M.Tabarant, B. Laurent – CEA Saclay (2015)

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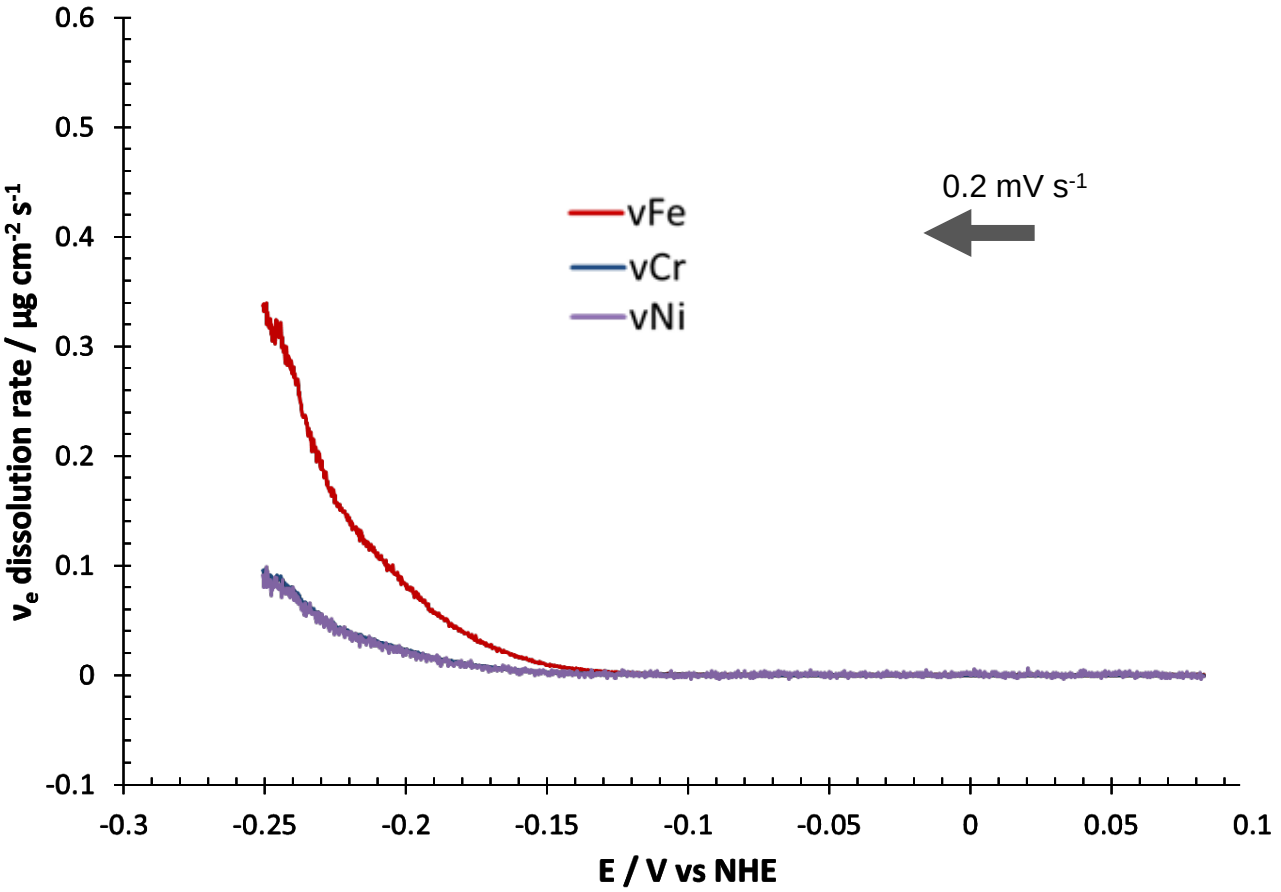


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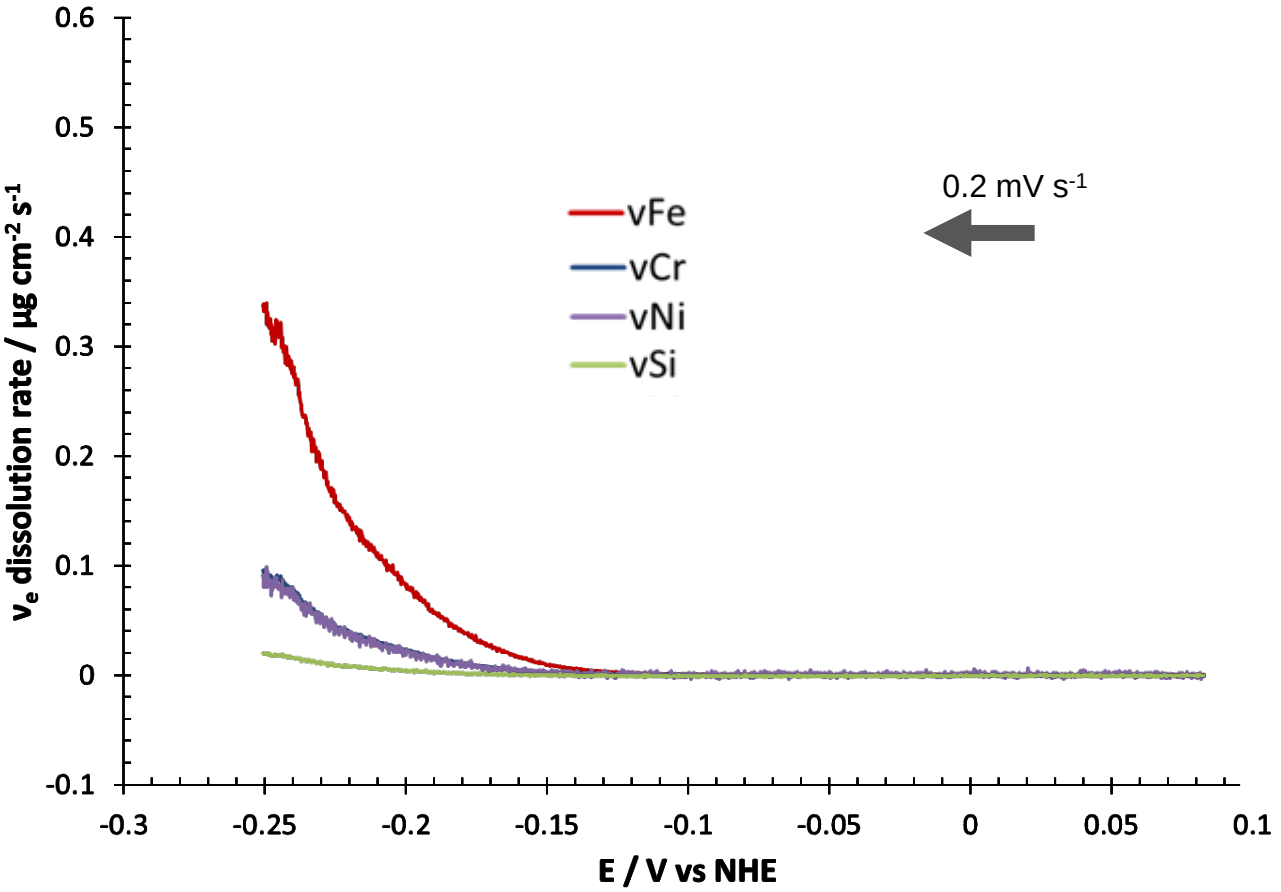


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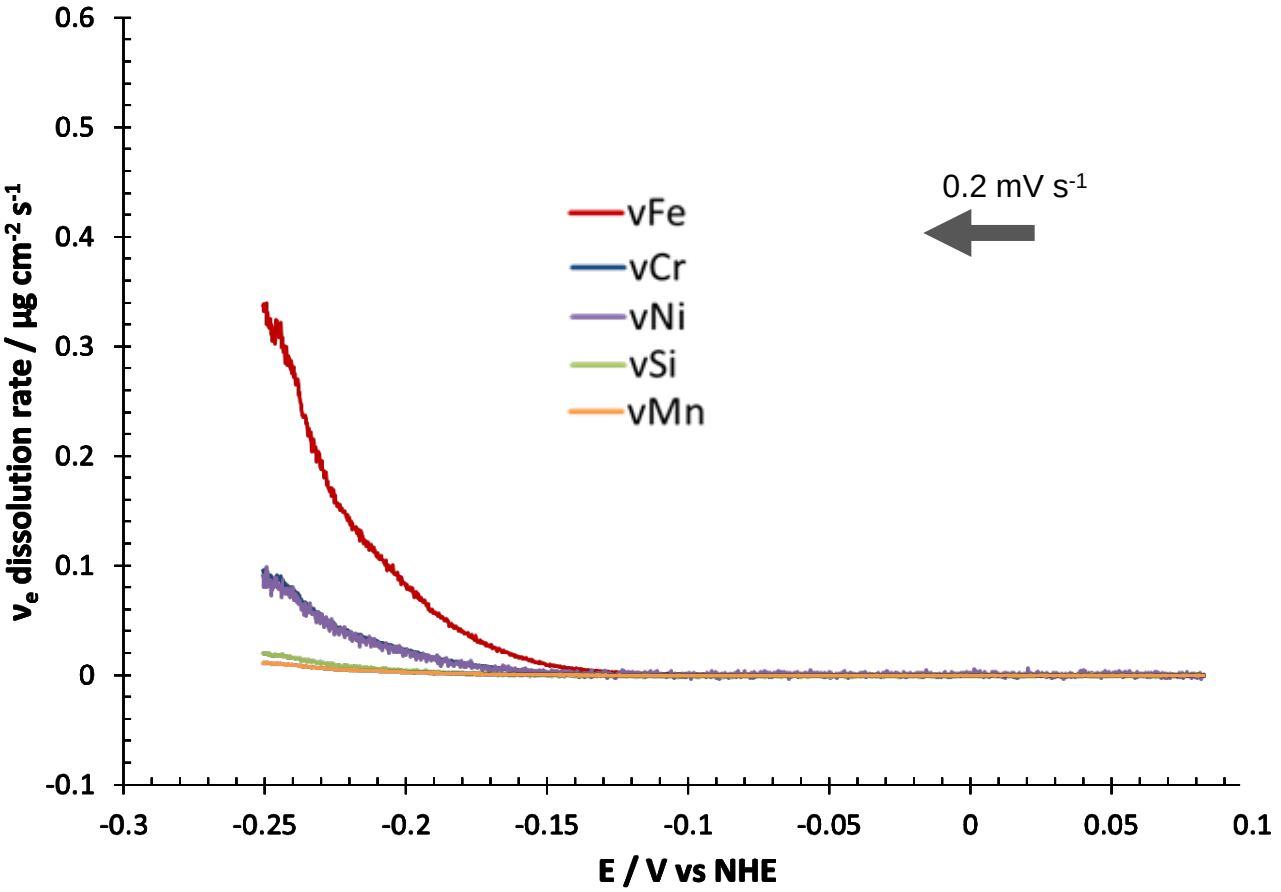


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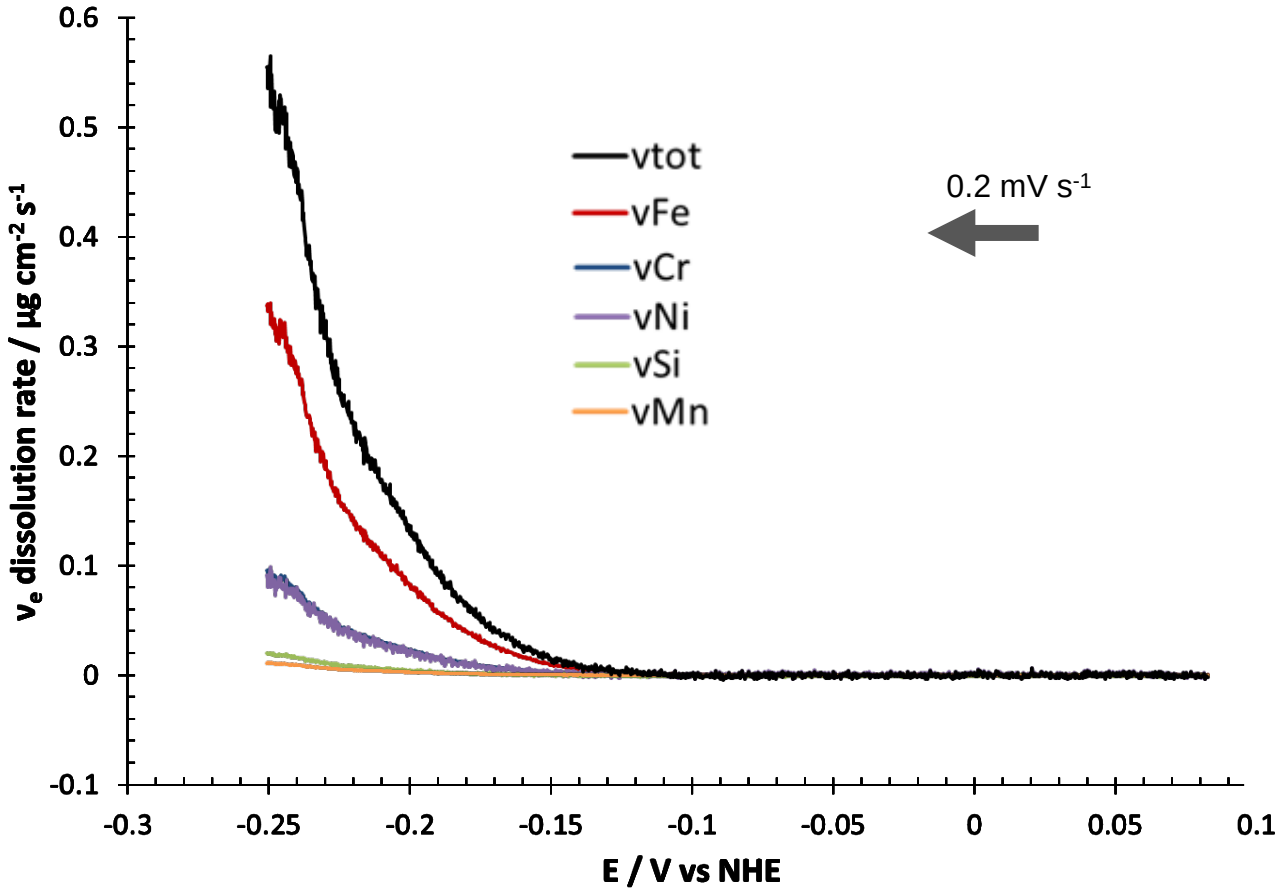


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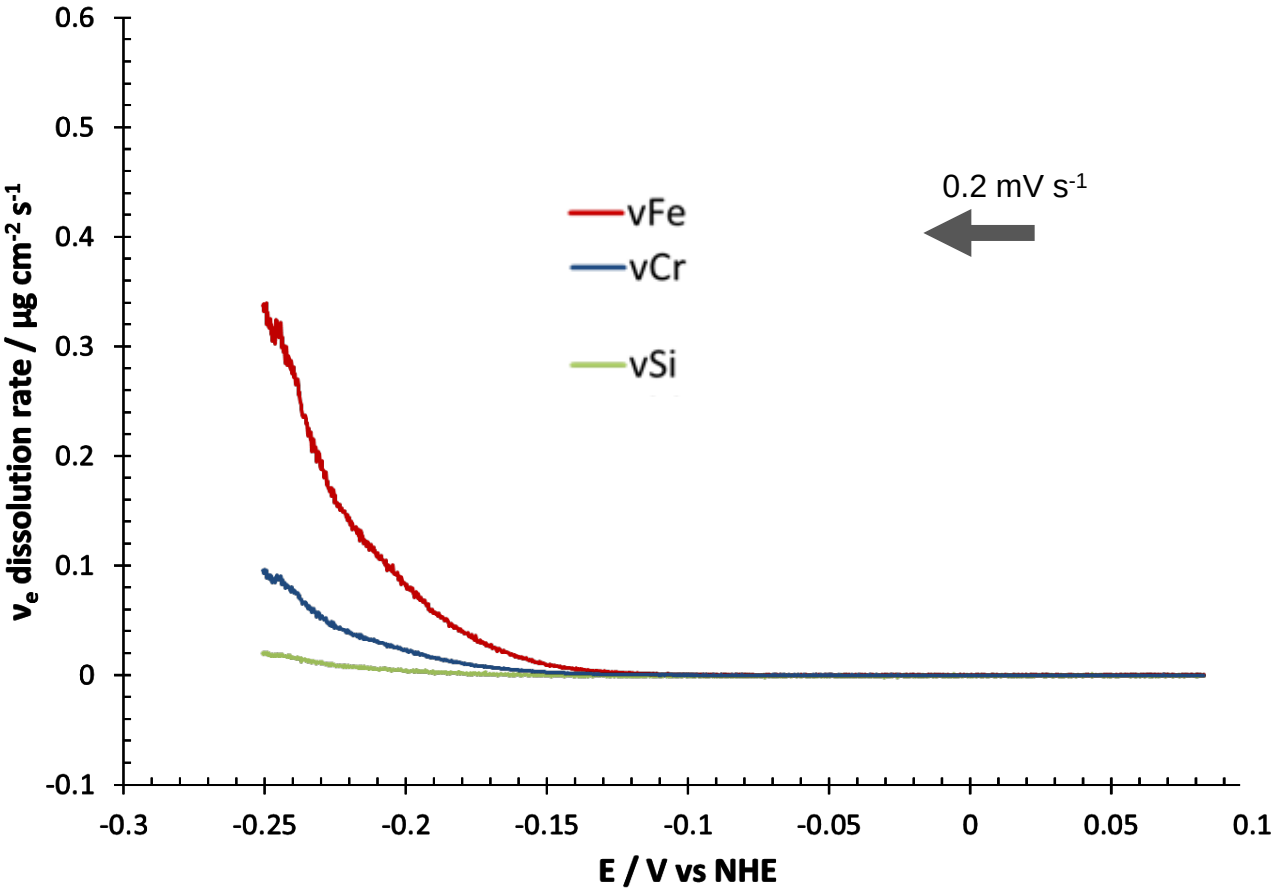


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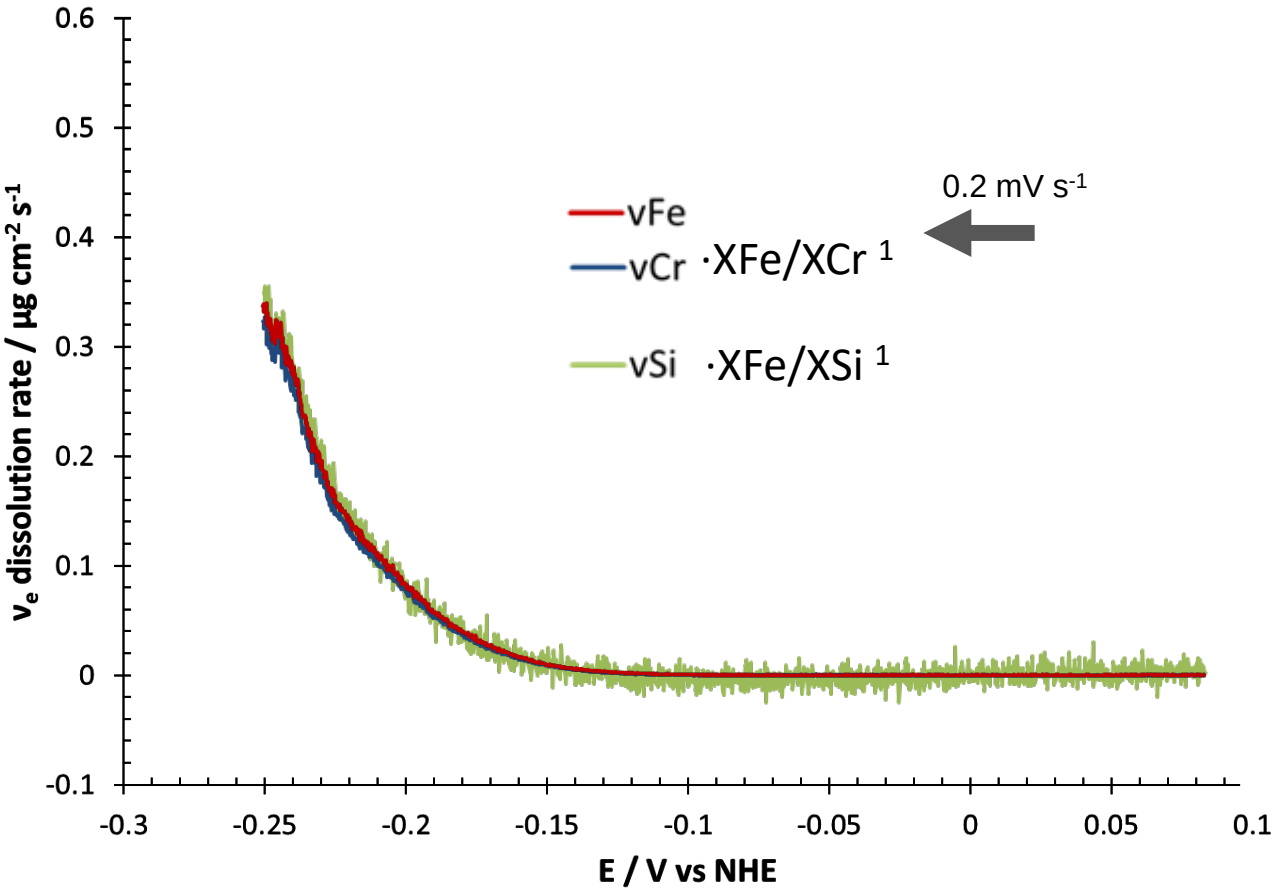


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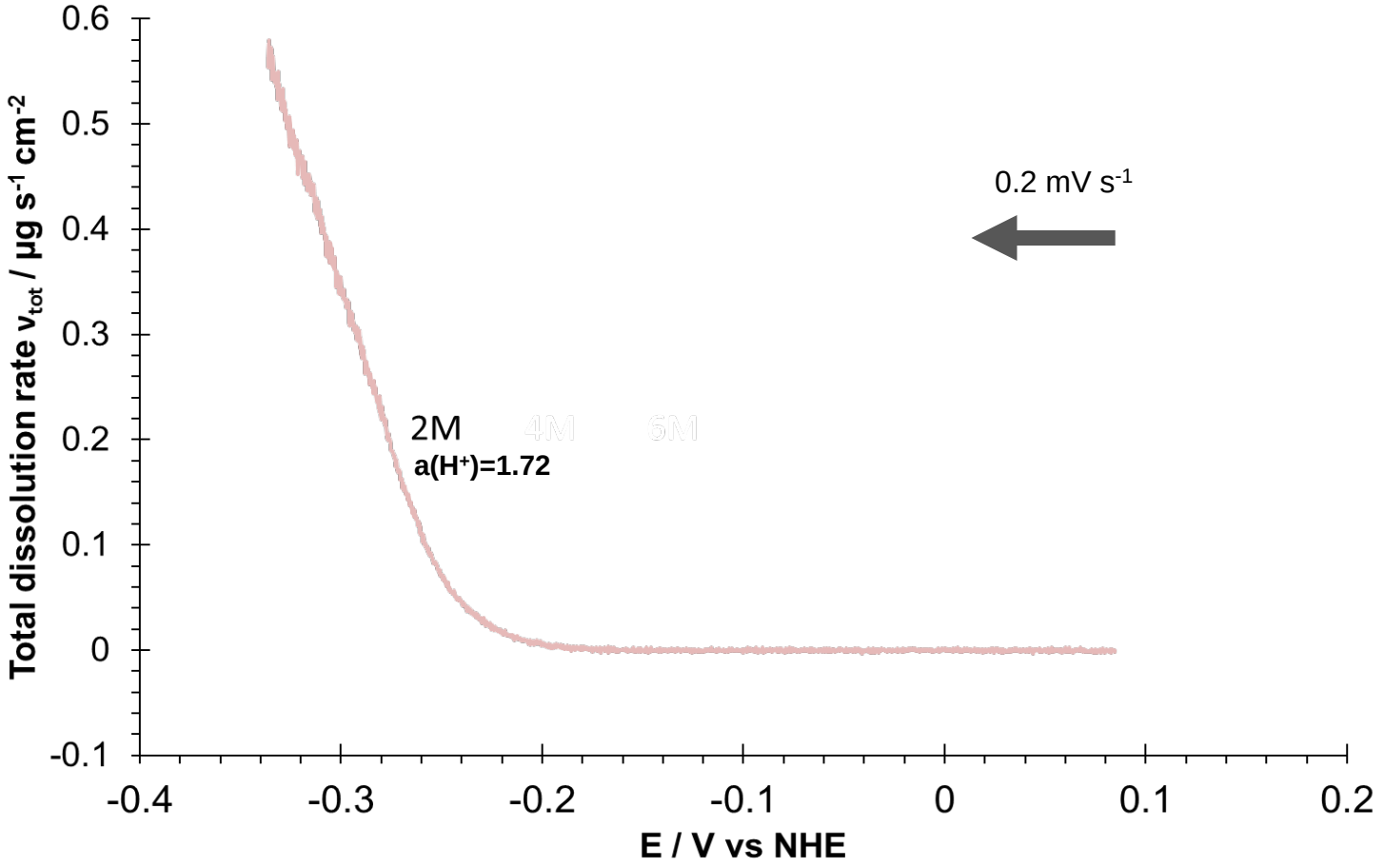


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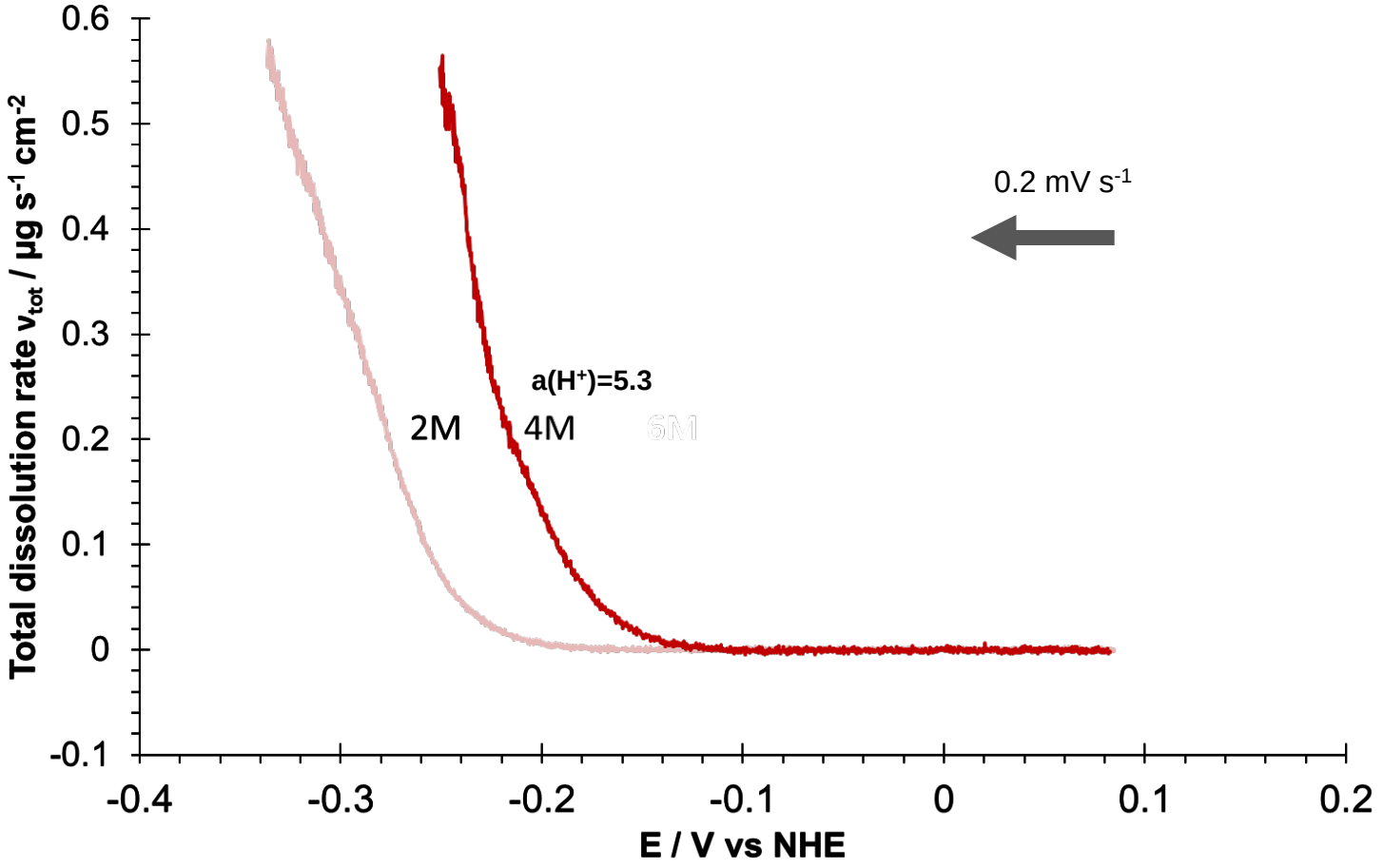
HOW DOES E_R VARY WITH $[HNO_3]$?

Silicon-rich stainless steel – HNO_3 – 28°C



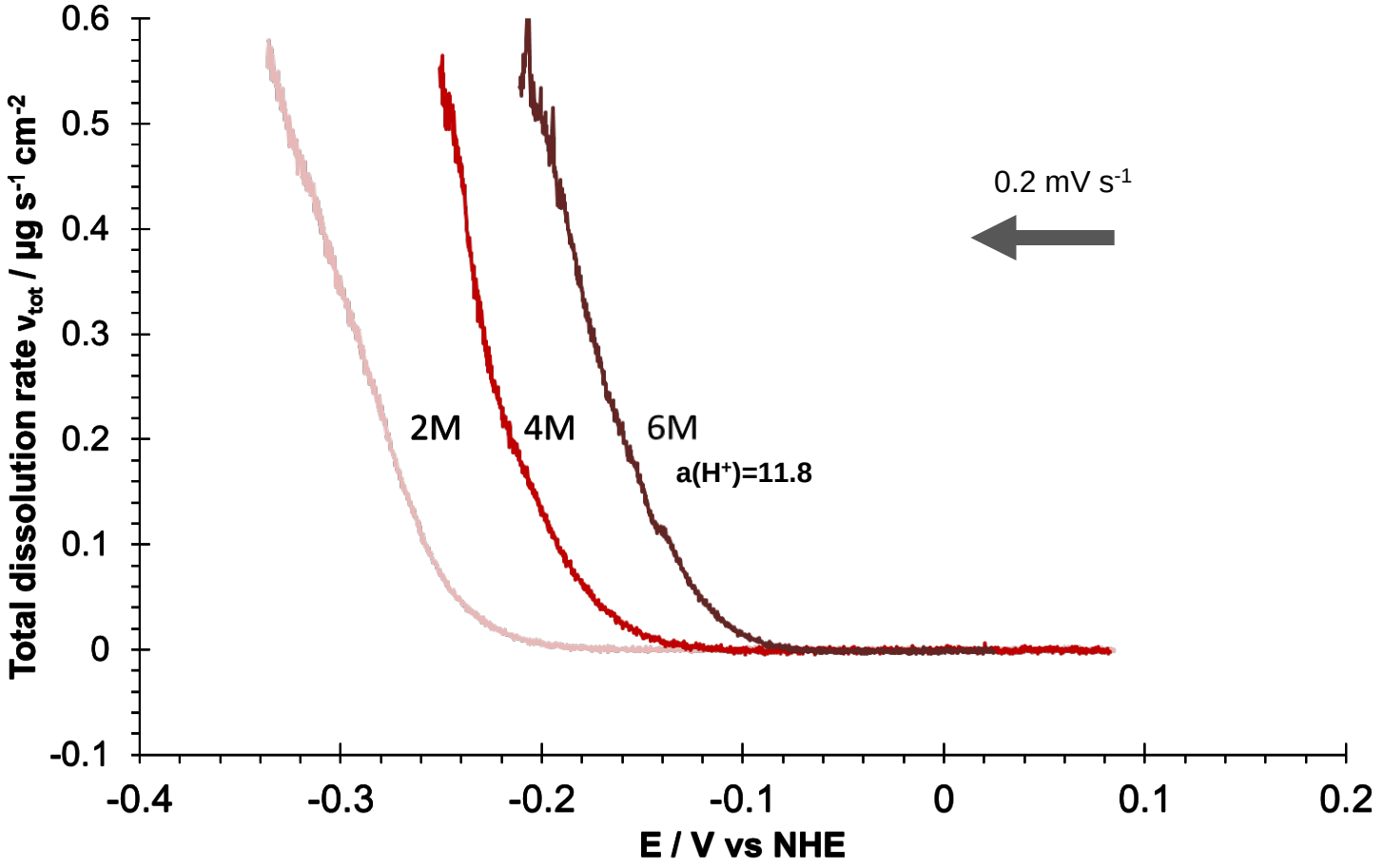
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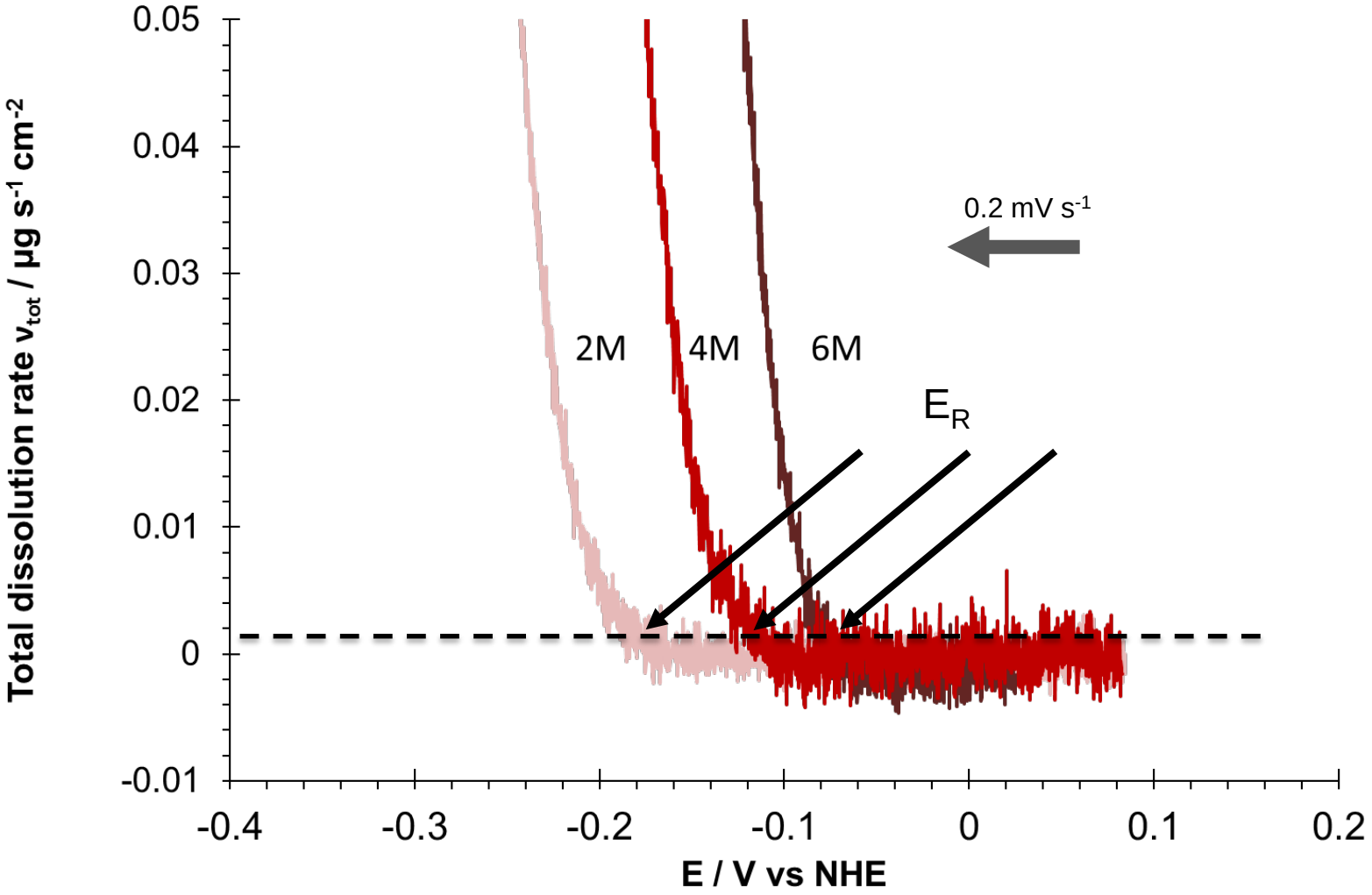
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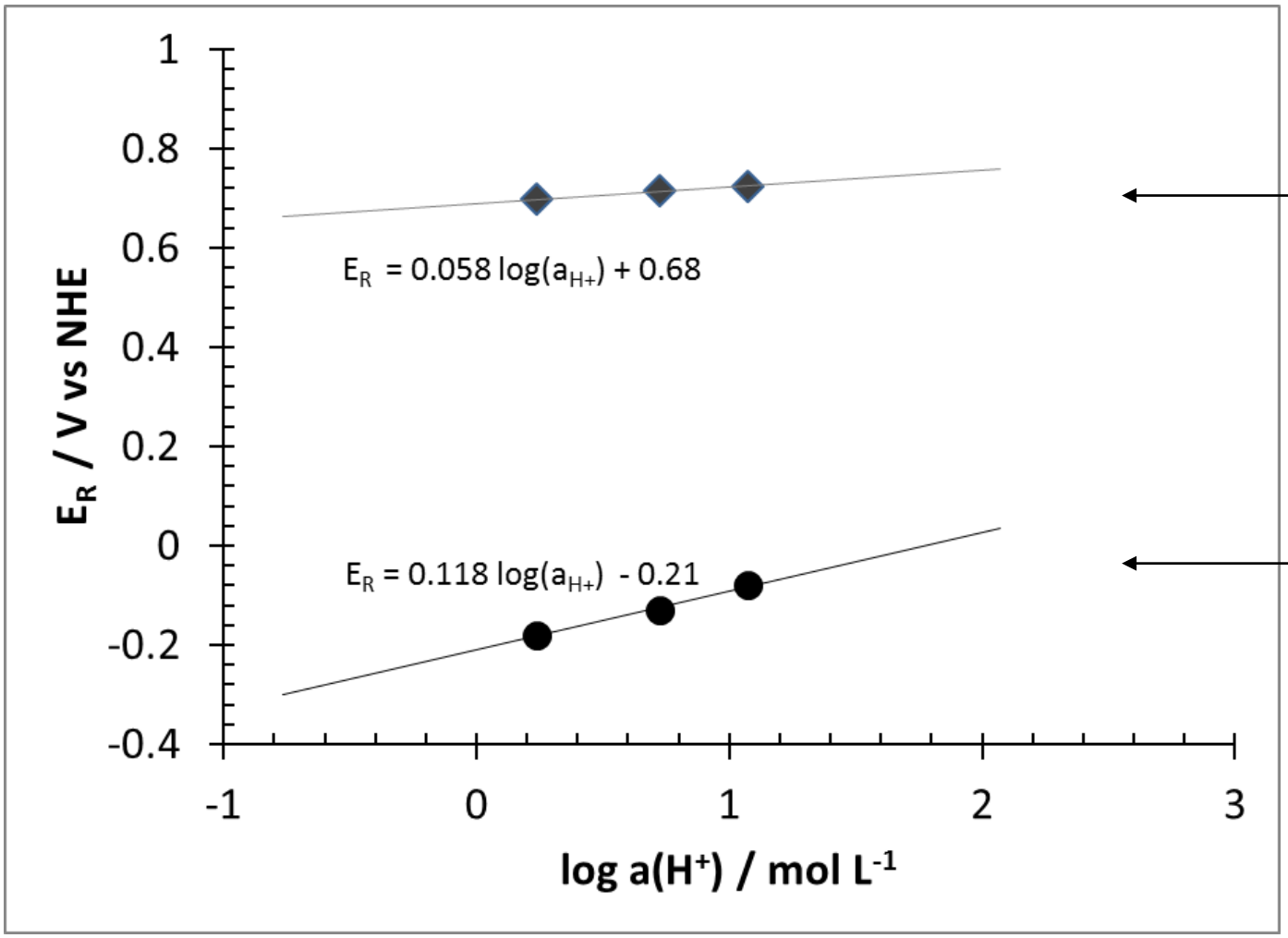


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HOW DOES E_R VARY WITH $[HNO_3]$?



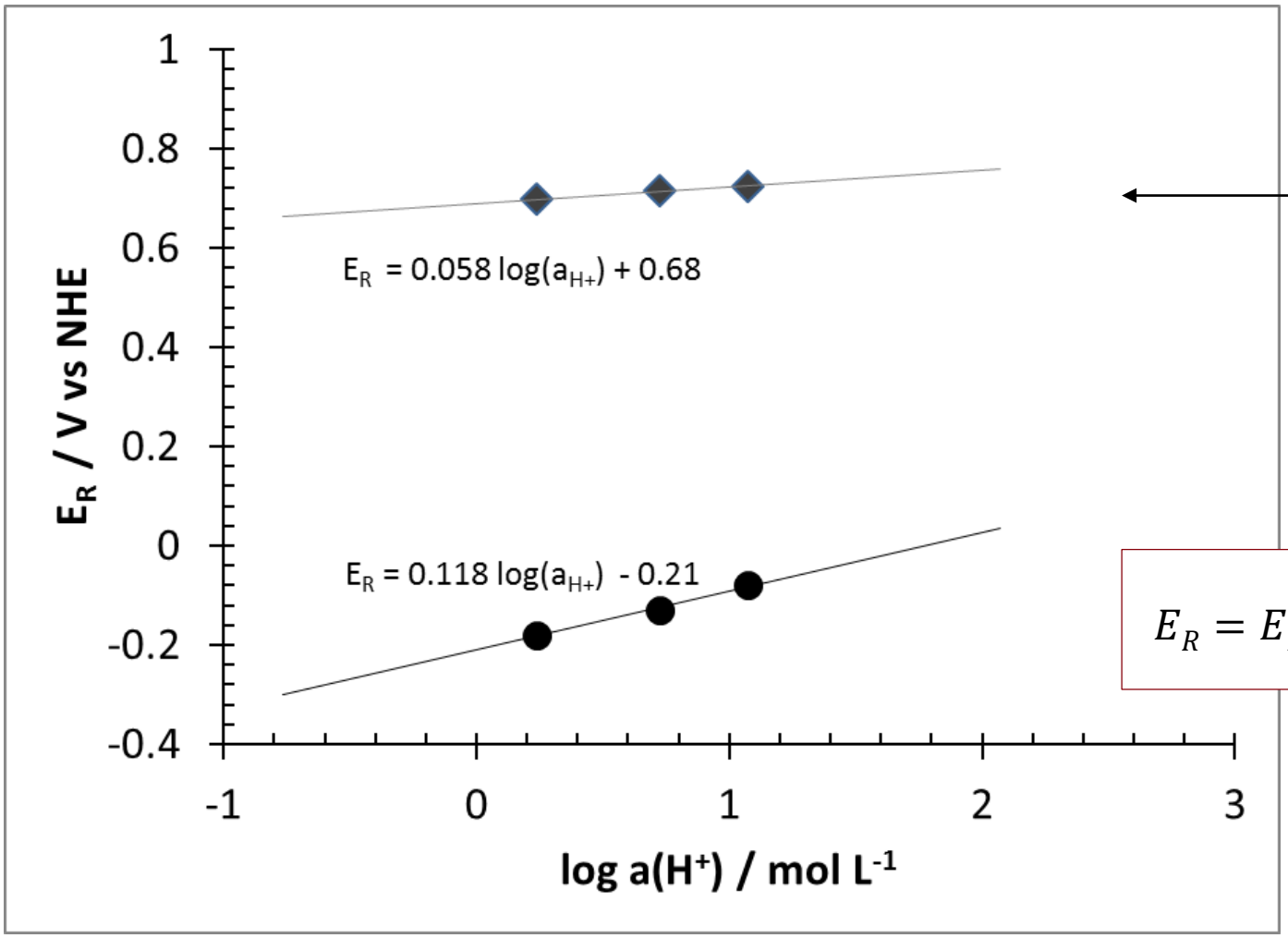
Pure Fe [1]

Si rich steel

[1] Rocha H-J. and Lennartz G. (1955). Archiv für den Eisenhüttenwesen **117**(933).

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HOW DOES E_R VARY WITH $[HNO_3]$?



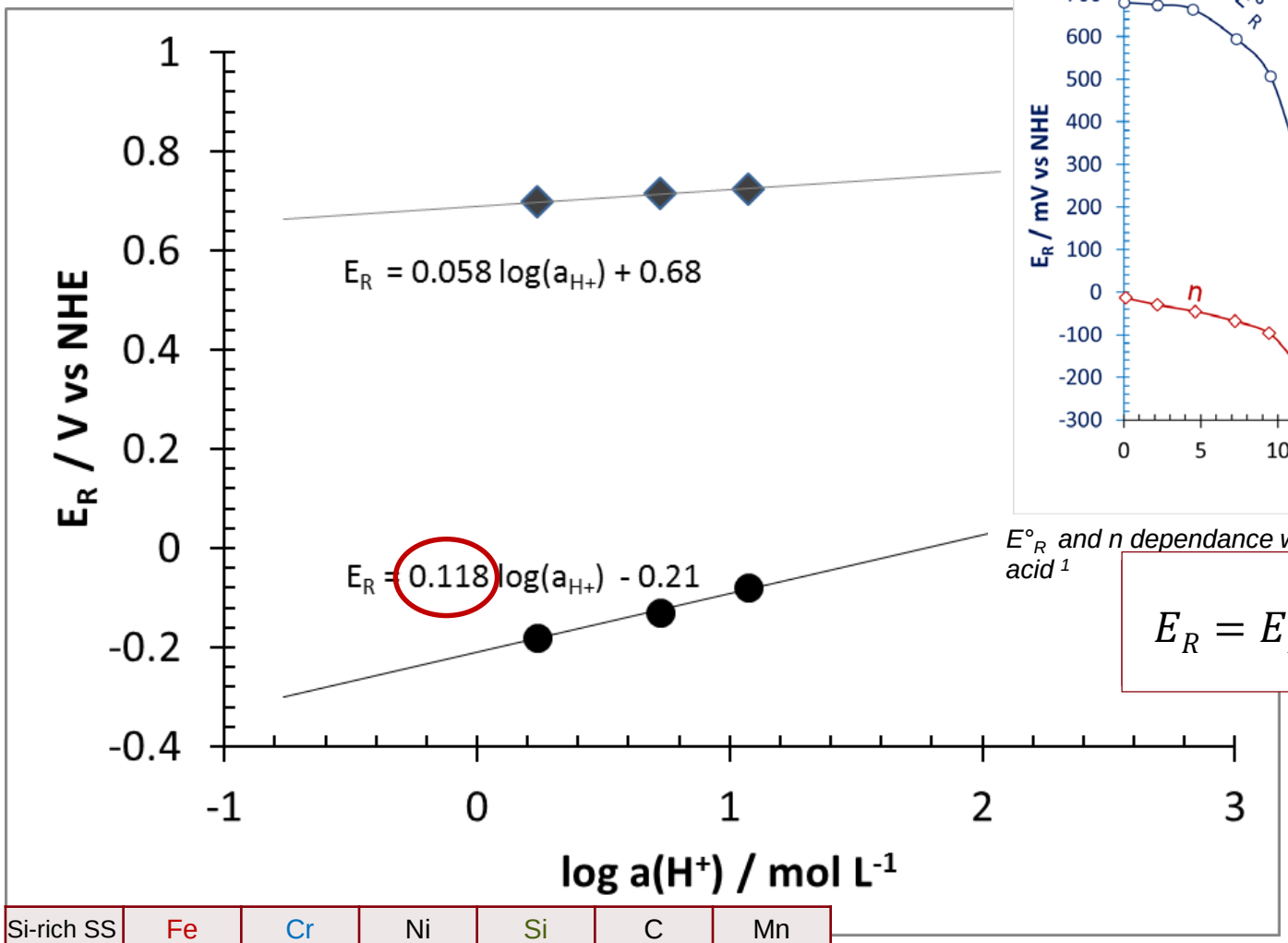
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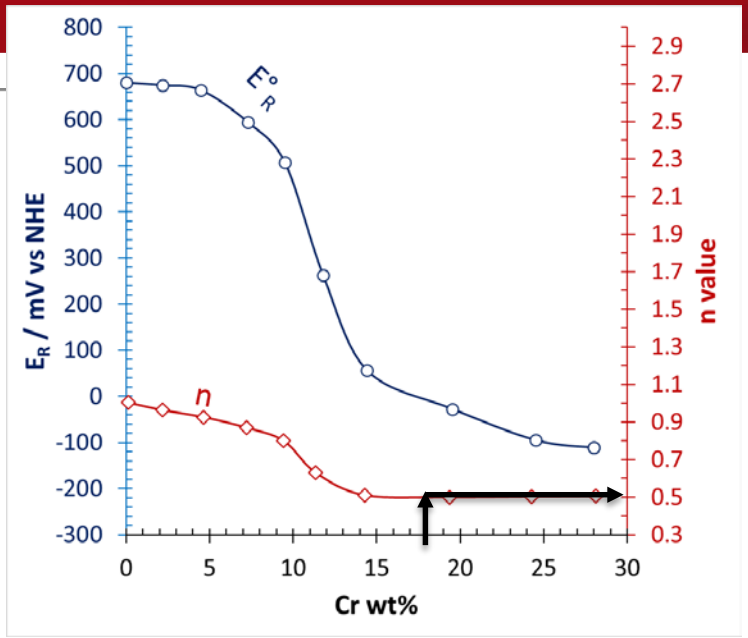
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.

HOW DOES E_R VARY WITH $[HNO_3]$?





$E°_R$ and n dependance with chromium amount in sulfuric acid [1]

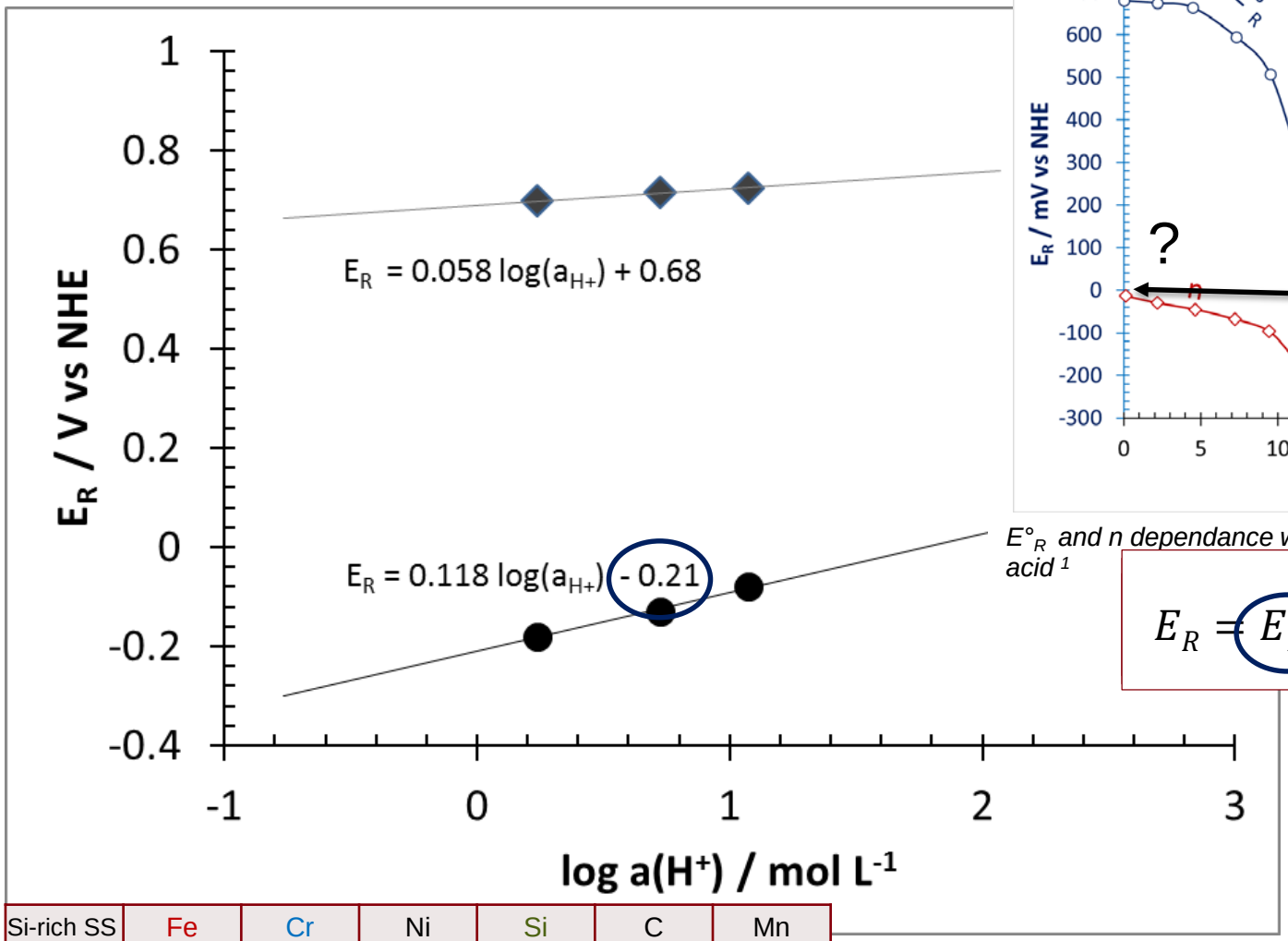
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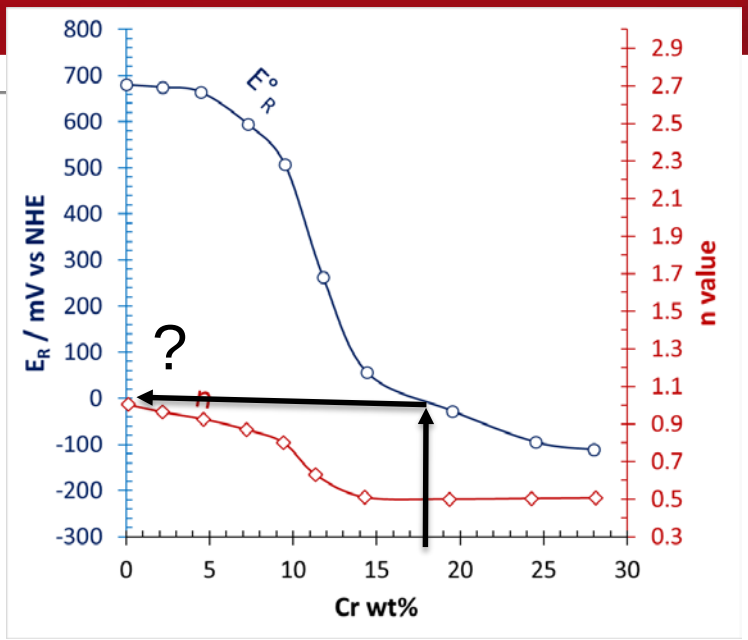
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HOW DOES E_R VARY WITH $[HNO_3]$?



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$E°_R$ VARIATION

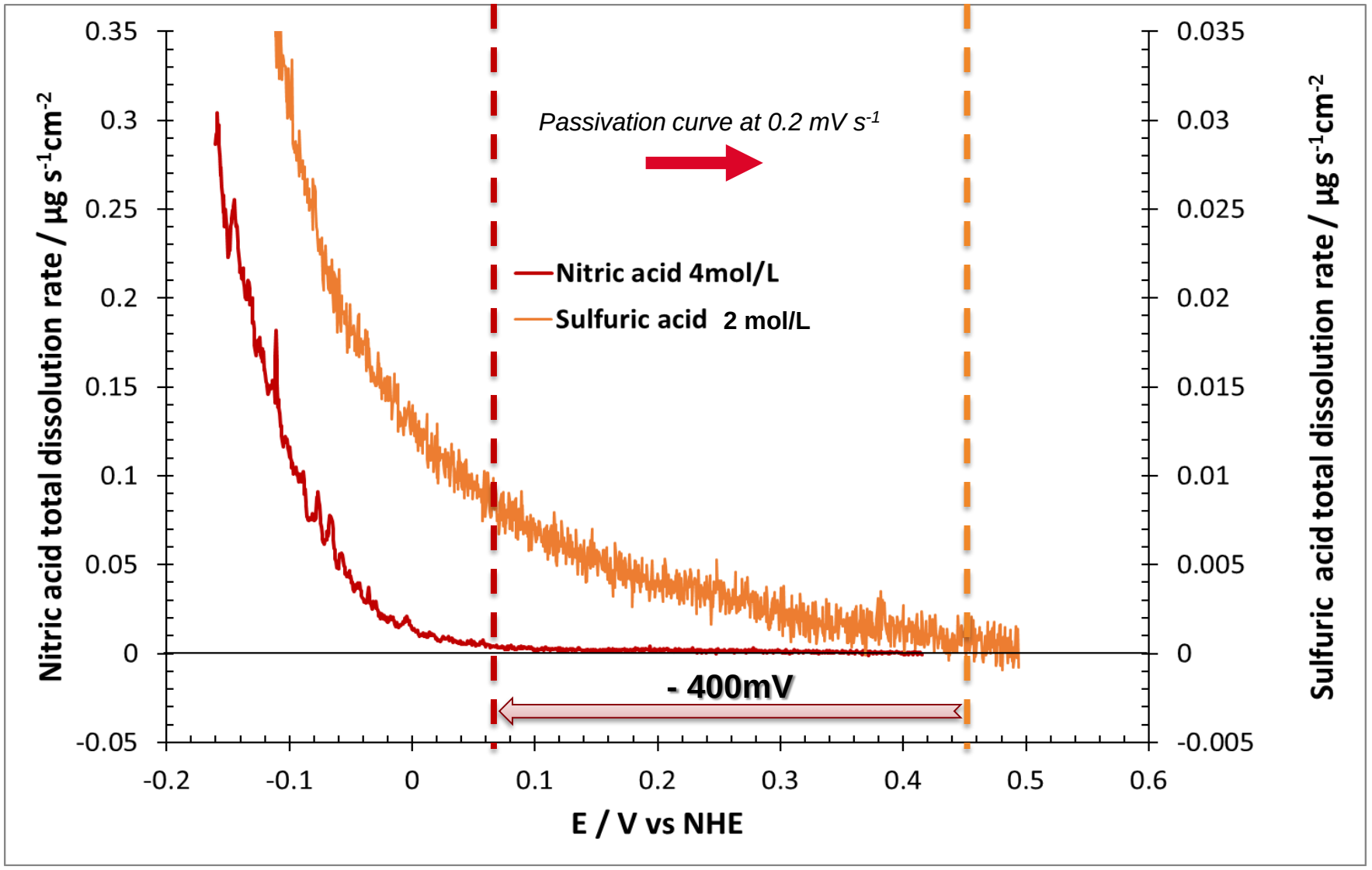
How to explain $E_R°$ variation ?

Two main factors might influence $E_R°$



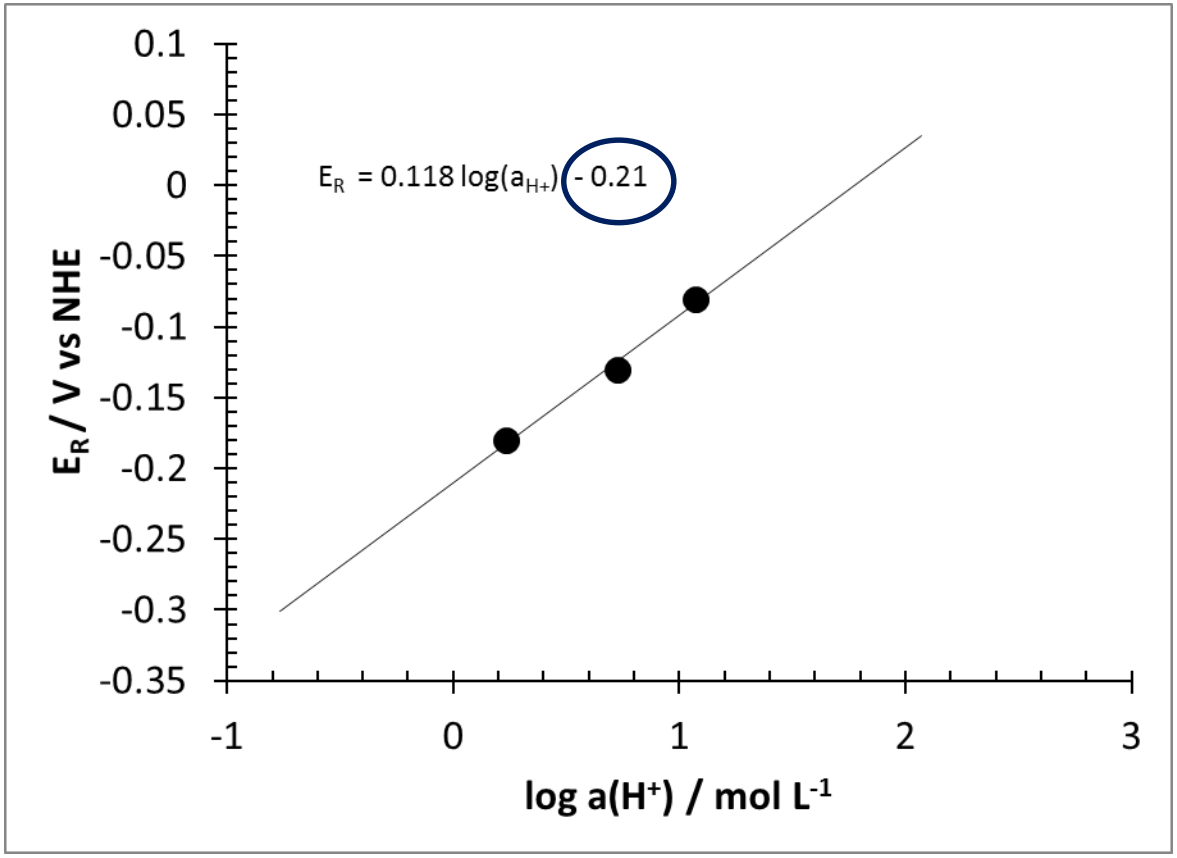
1. HOW DOES E_R VARY WITH NATURE OF ACID ?

HYPOTHESIS : E_R & E_P VARY WITH THE SAME SLOPE

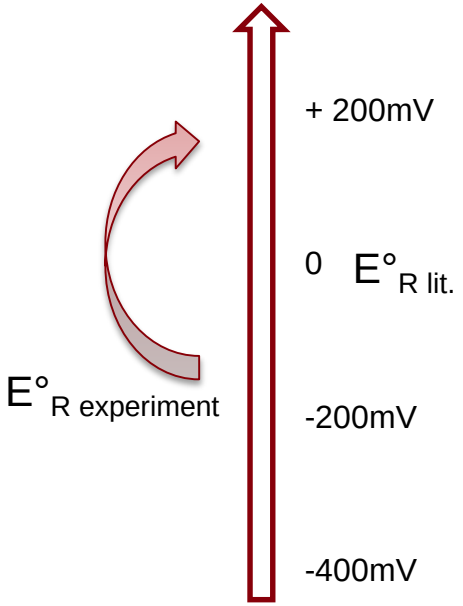


$E°_R$ VARIATION

How to explain $E_R°$ variation ?



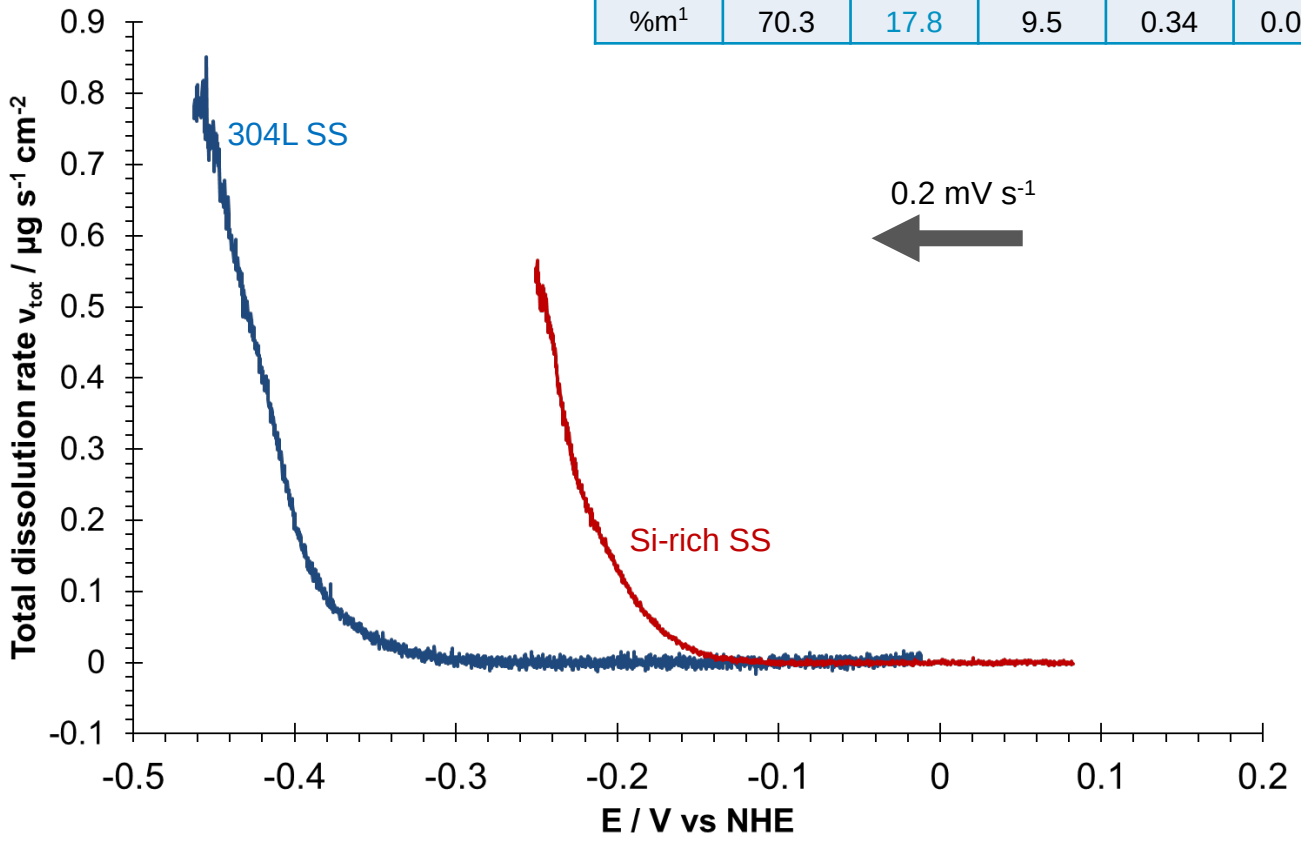
$E_R°$ remains high when compared to literature…



2. WHAT IS THE IMPACT OF SILICON ENRICHMENT ?

HNO_3 4M – 28°C

304L	Fe	Cr	Ni	Si	C	Mn
%m[1]	70.3	17.8	9.5	0.34	0.027	1.5



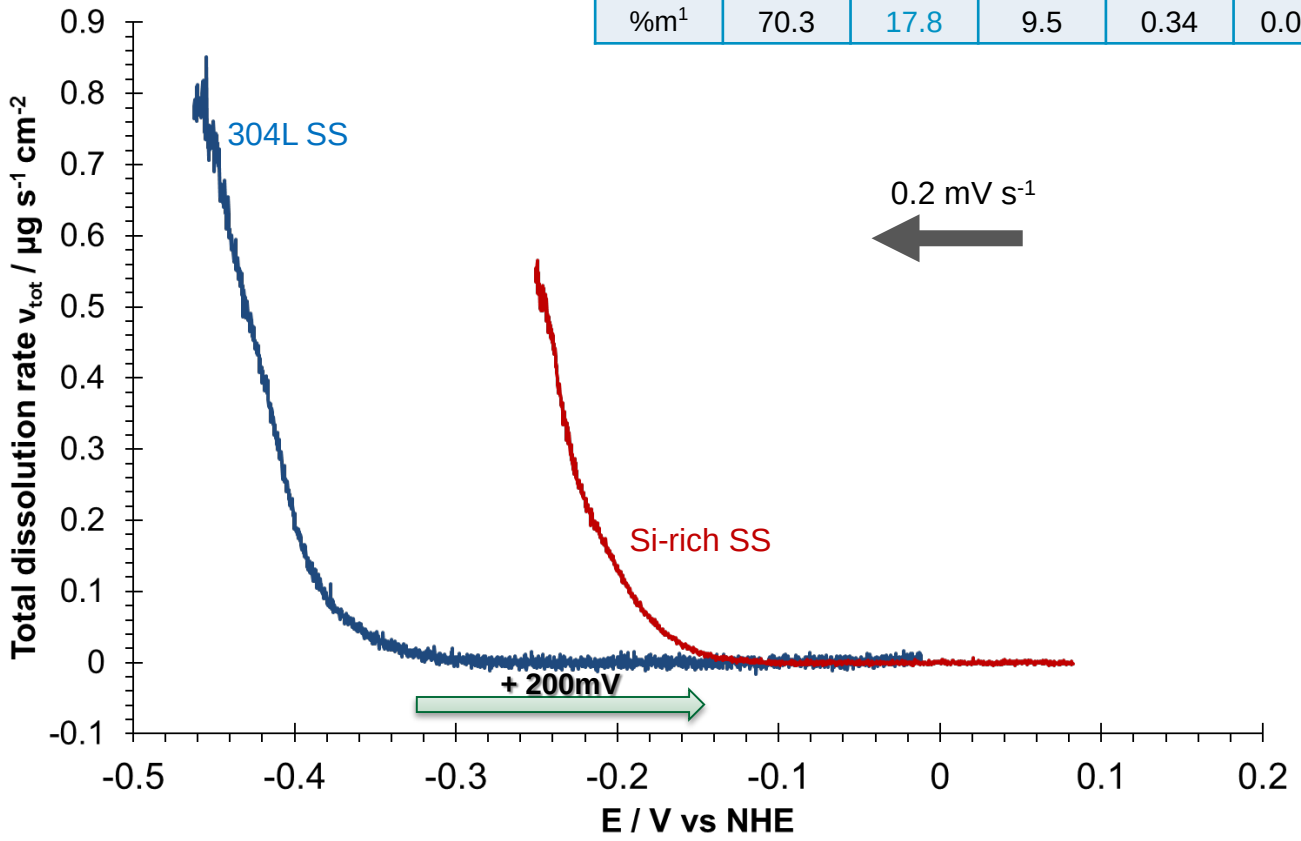
Si-rich SS	Fe	Cr	Ni	Si	C	Mn
%m[1]	59.8	18.8	15.1	3.6	0.029	1.9

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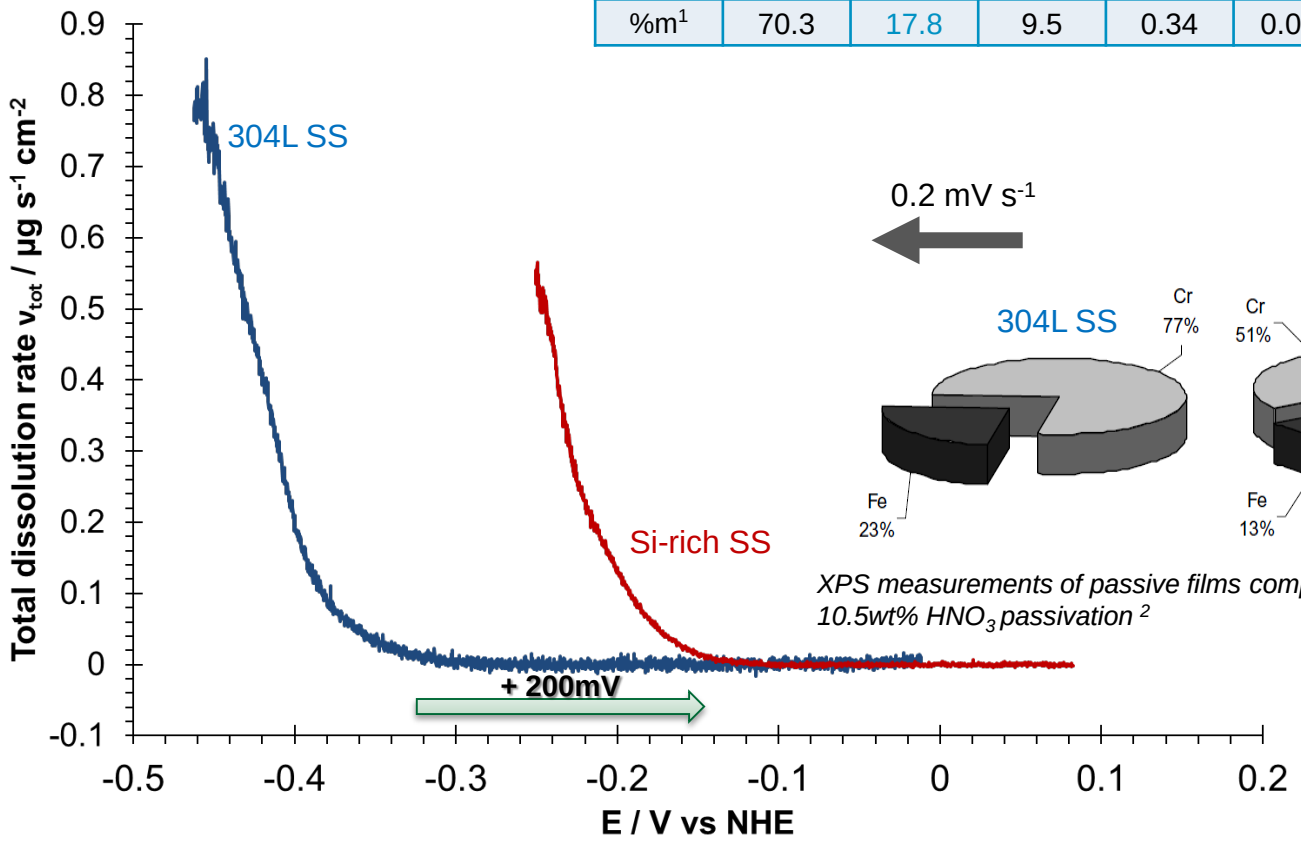
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XPS measurements of passive films composition (at.%) after 10.5wt% HNO_3 passivation [2]

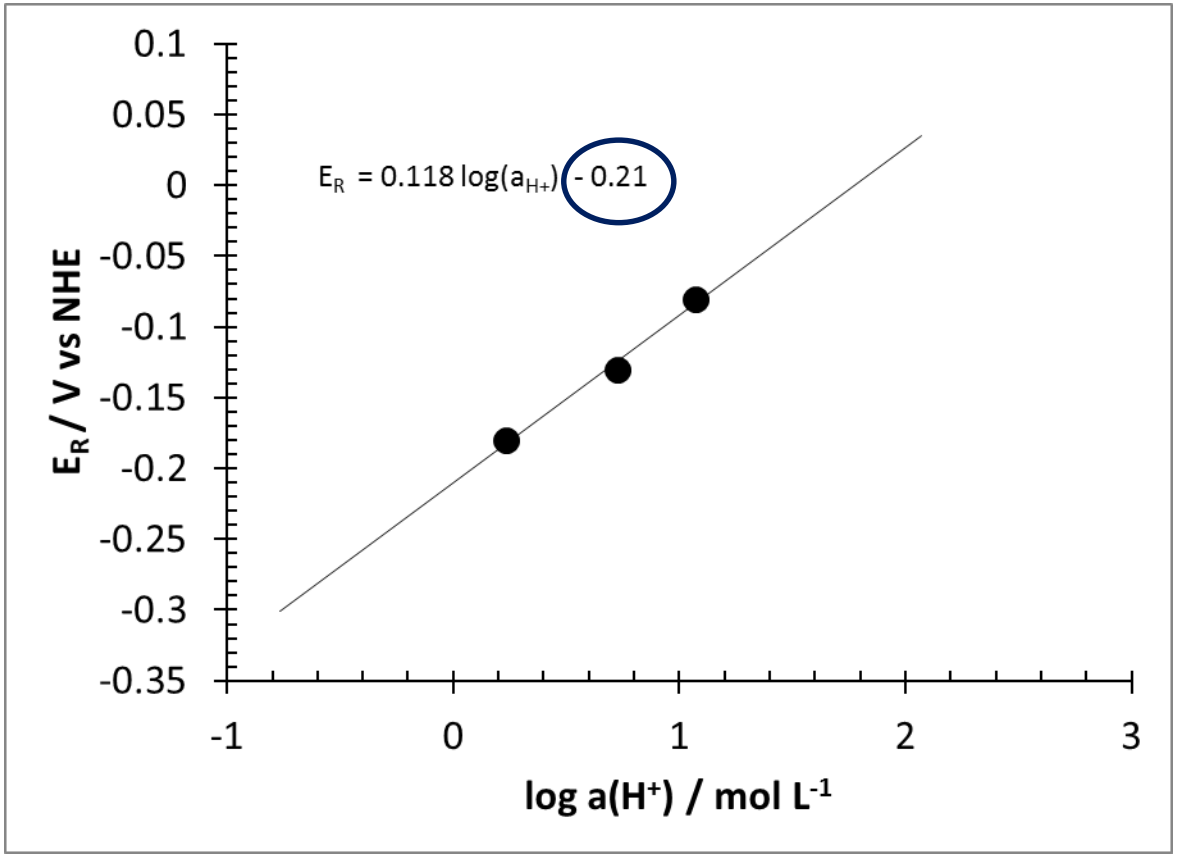
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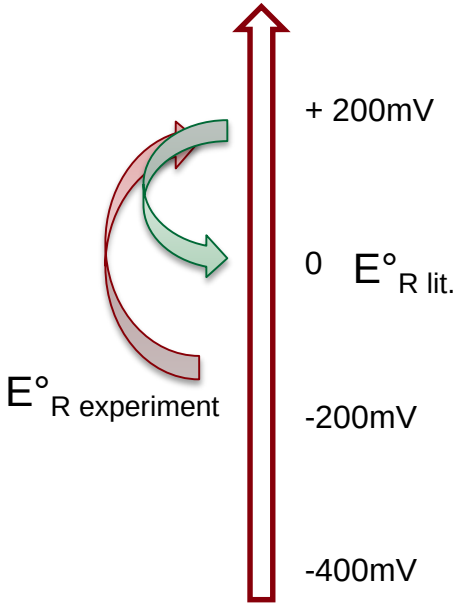
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[2] Robin, R., Miserque, F., *et al.* (2008). Journal of Nuclear Materials **375**(1): 65-71.

$E°_R$ VARIATION

How to explain $E_R°$ variation ?





CONCLUSION - OUTLOOK

Conclusion

- AESEC technique made possible HNO_3 in situ measurements of the E_R potential and reveal different passive layer characteristics depending on [HNO_3]

- Following have to be taken into account :
  - Nitric acid media impact
  - Metallurgy of the studied steel :
    Silicon in the passive layer (~ 36%$_{at.}$) → easiest passive layer to dissolve

- Research in progress : linear dependance on temperature
  - Such steel are designed for higher temperatures
  - AESEC membrane and cell can hold up to 80°C

Thank you for your attention !

Special thanks

Bataillon C., Benoit M., Bigot M., Brijou-Mokrani N., Cavaliere N., Fallet A., Fauvet P., Geneve O., Gharbi O., Han J., Heurthault S., Keddam M., Laghoutaris P., Pasquier-Tilliette S., Puga B., Rivollier M., Robin R., Shkirskij V., Soulié V., Zhou P.

The industrial partner

AREVA

Chimie Paris

ParisTech

PSL RESEARCH UNIVERSITY

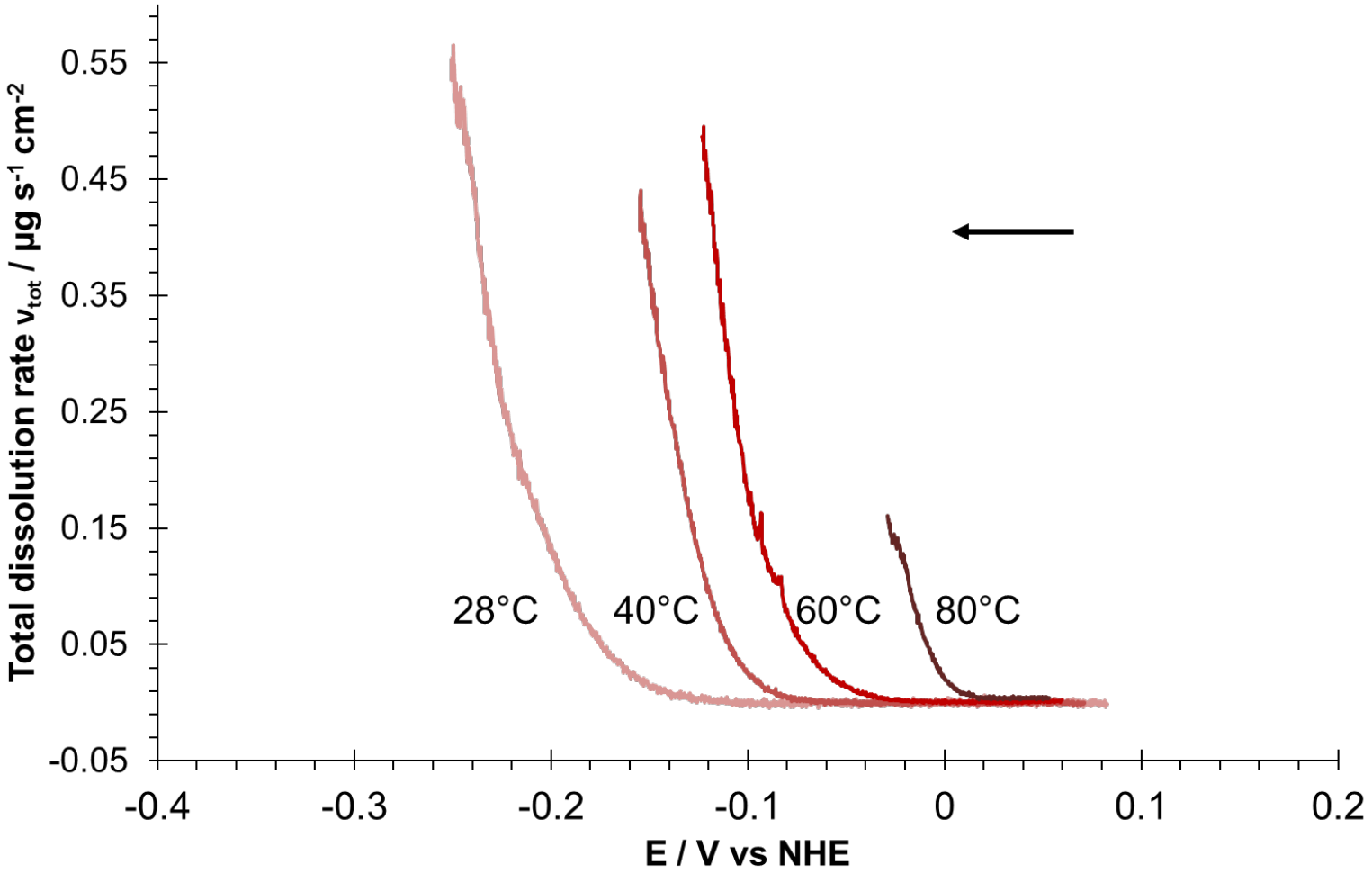
Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 XX XX XX XX | F. +33 (0)1 XX XX XX XX

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REACTIVATION OF THE STEEL (VS T°)

Silicon-rich stainless steel – HNO_3 4M – 28°C



REACTIVATION OF THE STEEL (VS T°)

Silicon-rich stainless steel – HNO_3 4M – 28°C

