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How do $Co^{2+}_{(aq)}$ and $Zn^{2+}_{(aq)}$ interact with spinel in BWR coolant?

Recent progresses in fundamental understanding of radioactive cobalt induced radiation field and its suppression by zinc injection

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The following researchers at the Department of Chemistry and Chemical Engineering, Chalmers University of Technology have performed this work. Swedish Radiation Safety Authority and Swedish Nuclear Power Utilities provided the financial support. For further reading on the topics, please refer to *J. Nuc Mater. 540 (2020) 152361.*

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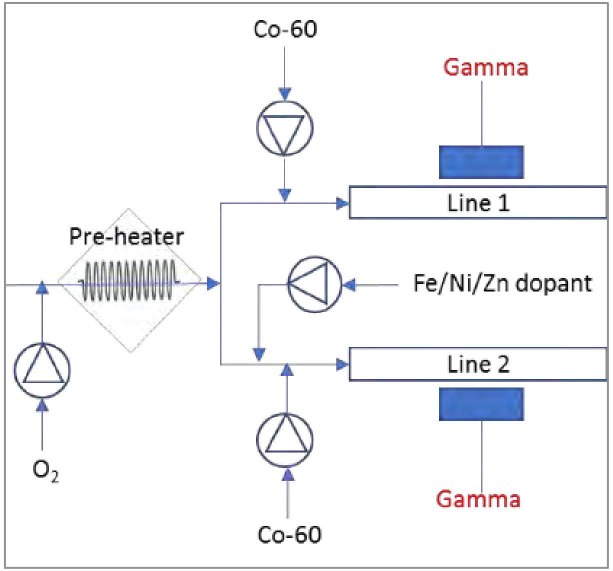
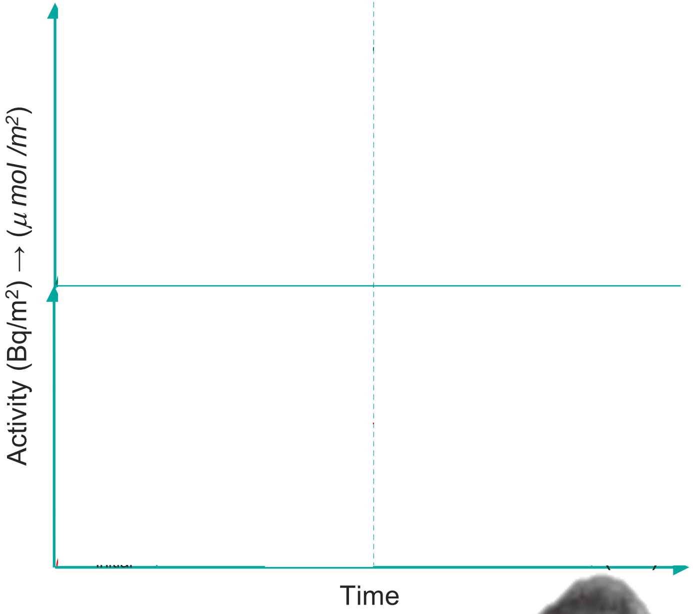
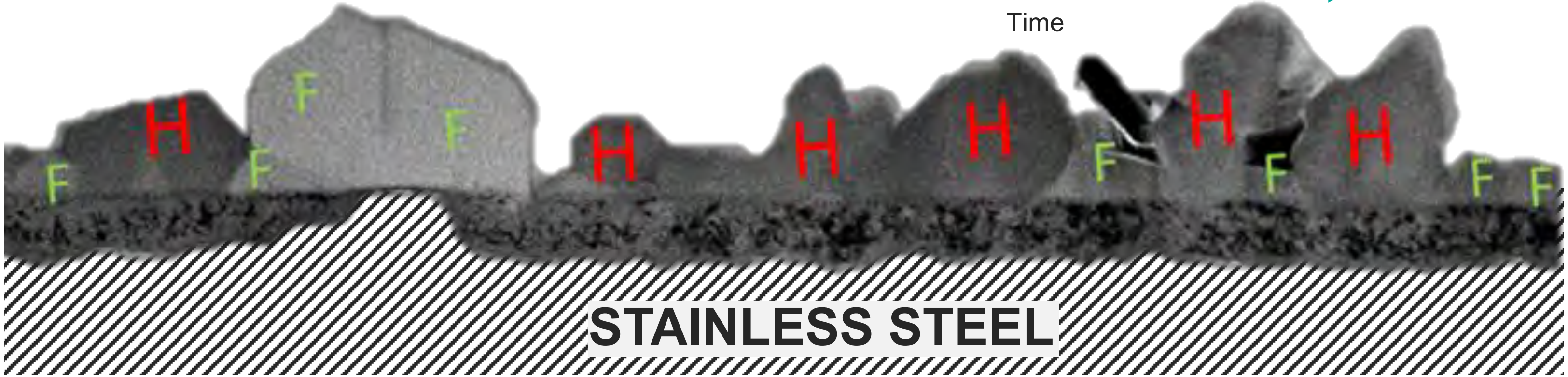
Outline

- Experimental/plant observations
- Hypotheses
- Interrogation (quantum chemistry)
- Summary of mechanisms


Co-60
Gamma
Line 1
Pre-heater
Fe/Ni/Zn dopant
Line 2
O_2
Gamma
Co-60


Activity (Bq/m^2) → (μ mol /m^2)
Time


F
H
F
F
F
H
H
H
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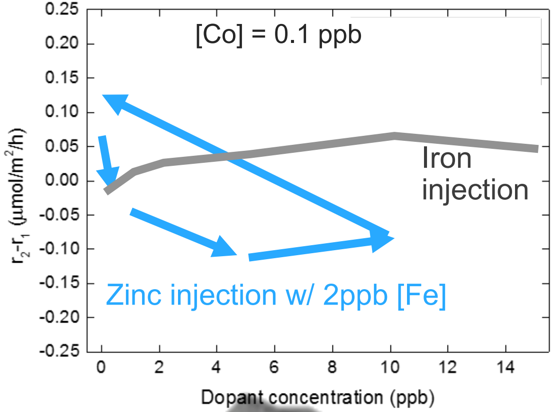
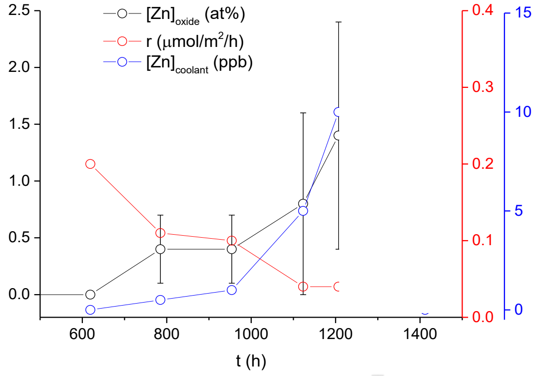
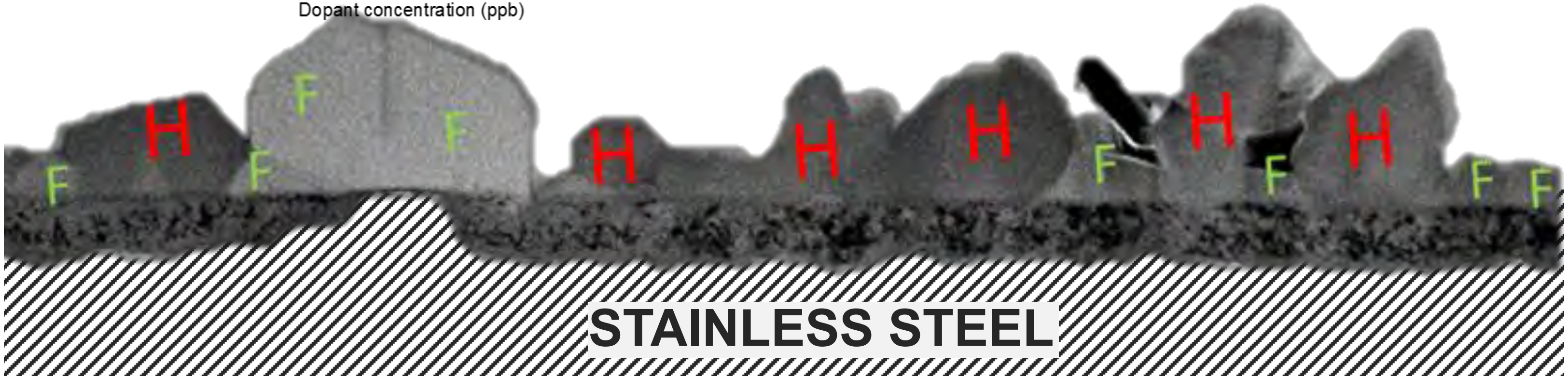
F
STAINLESS STEEL

Co-60 deposition rate

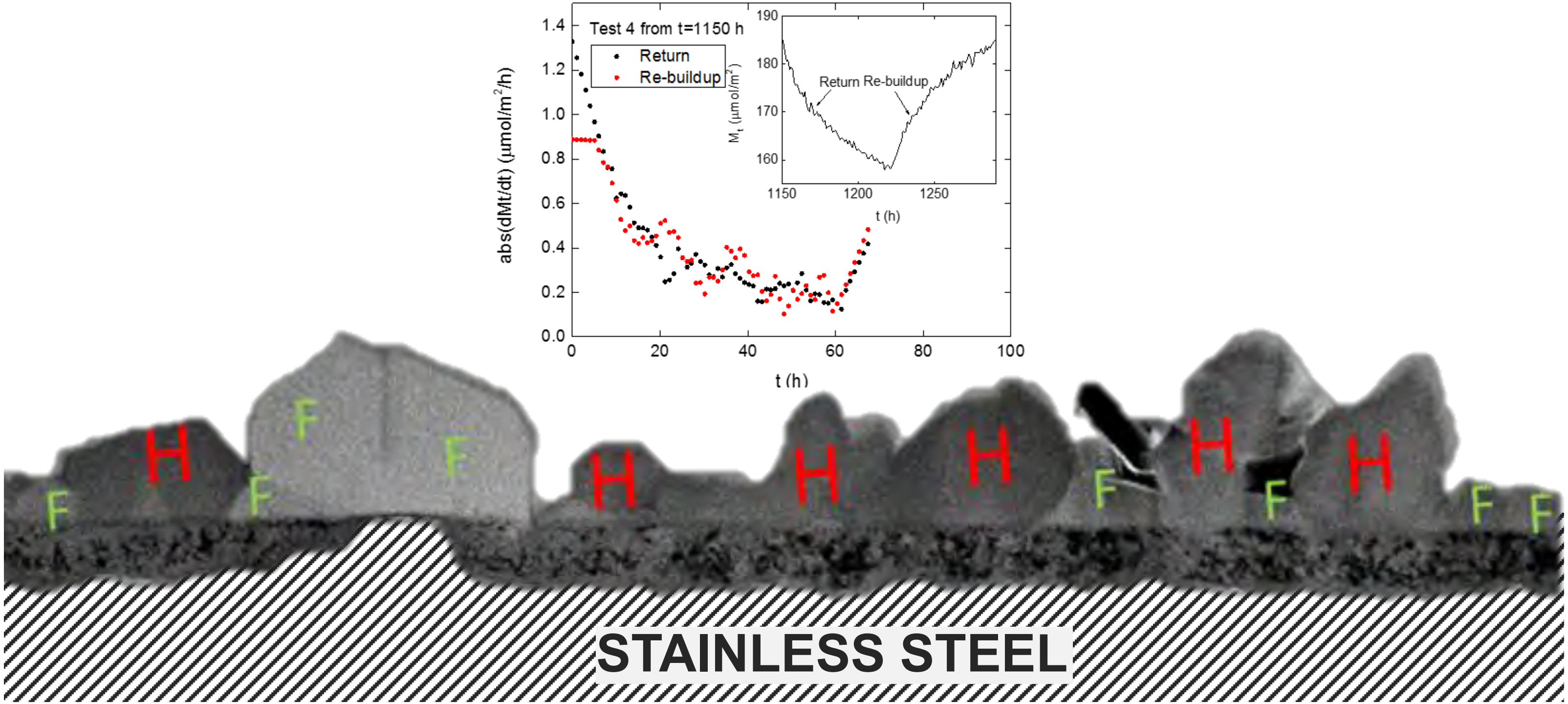
- Little effect by [Fe] in coolant
- Large effect by [Zn] in coolant (up to 5 ppb)



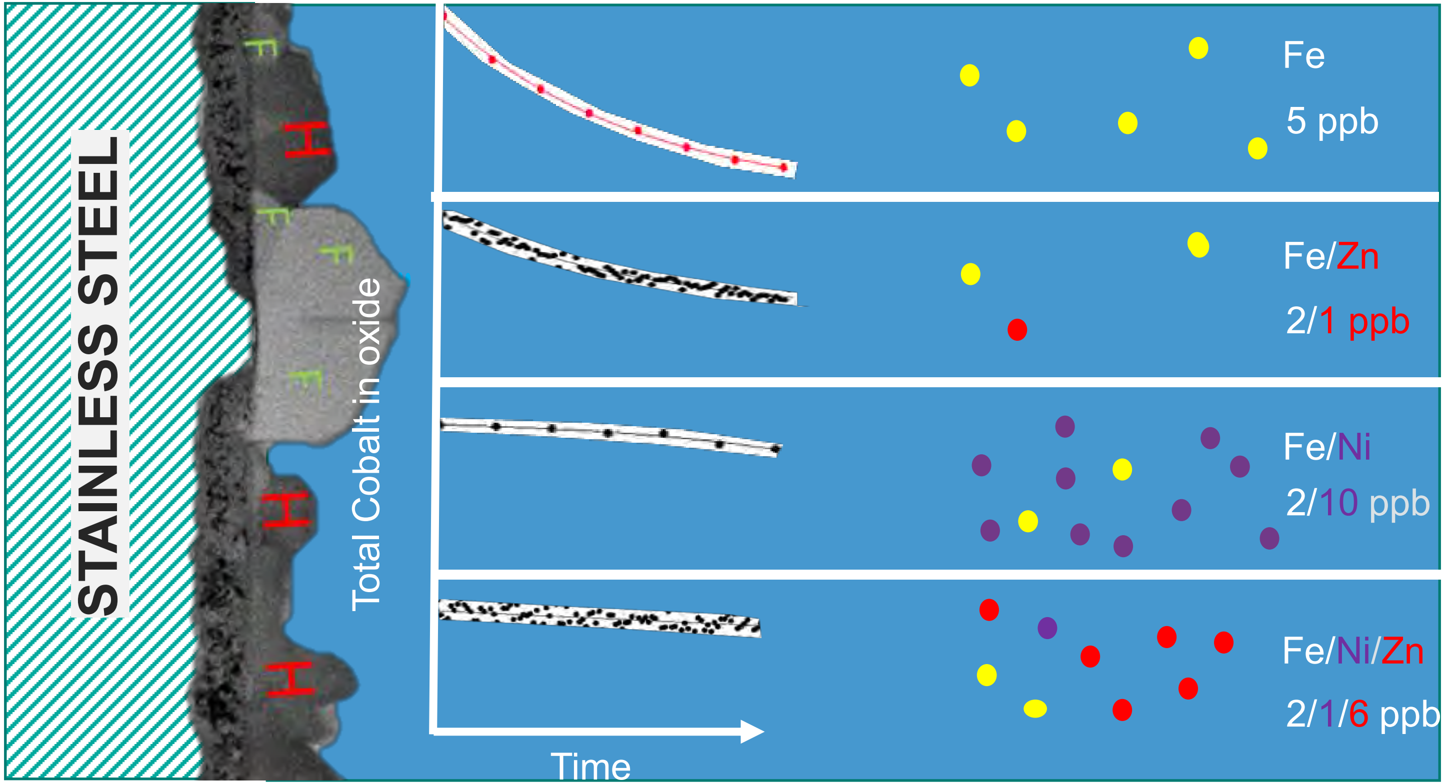




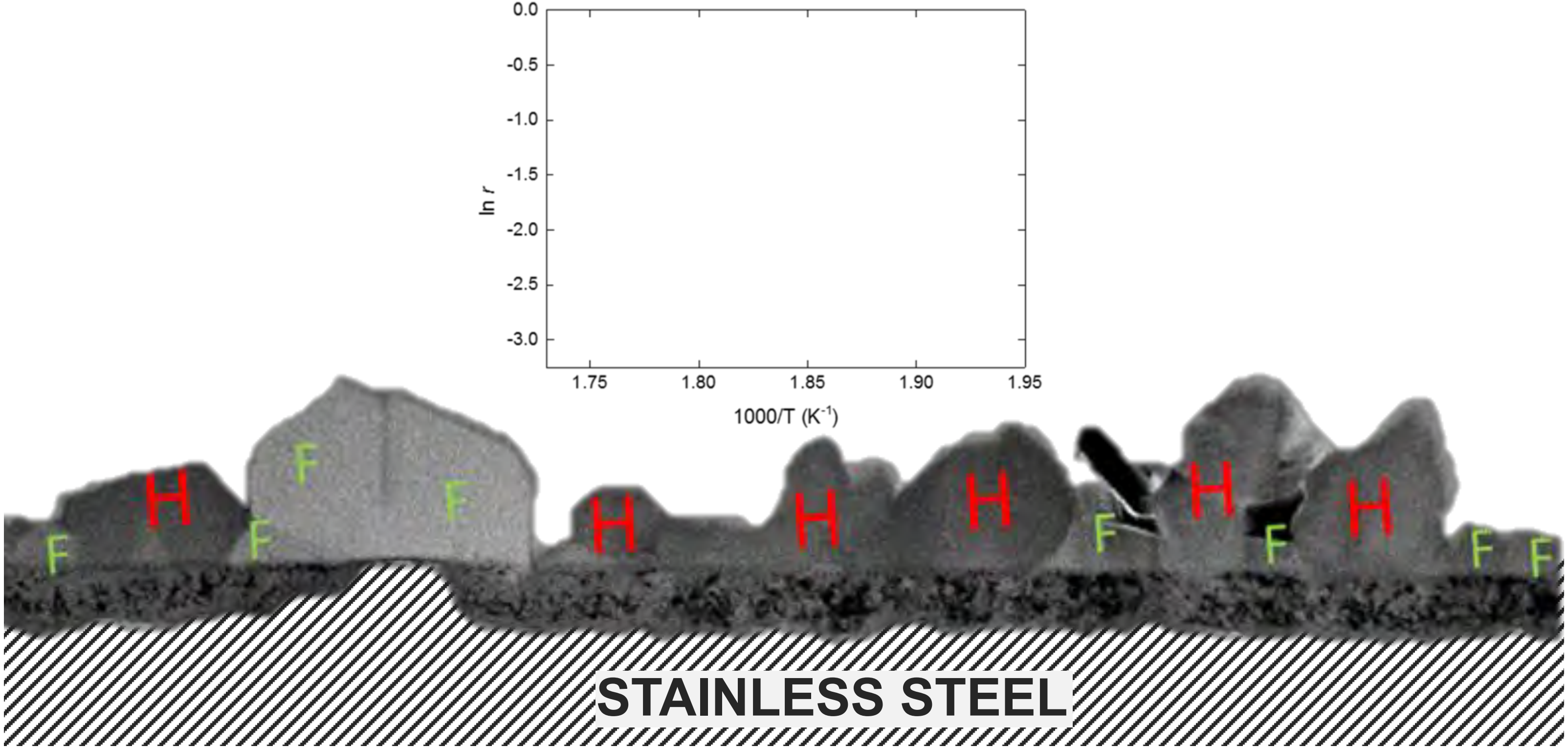
Co-60 deposition and release are reversible



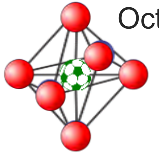
Co-60 release can be "blocked" by [$Ni^{2+}_{(aq)}$] and [$Zn^{2+}_{(aq)}$] but not by [Fe_{tot}]

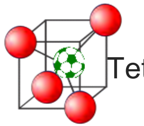


E_a=1 eV for Co deposition on oxide film

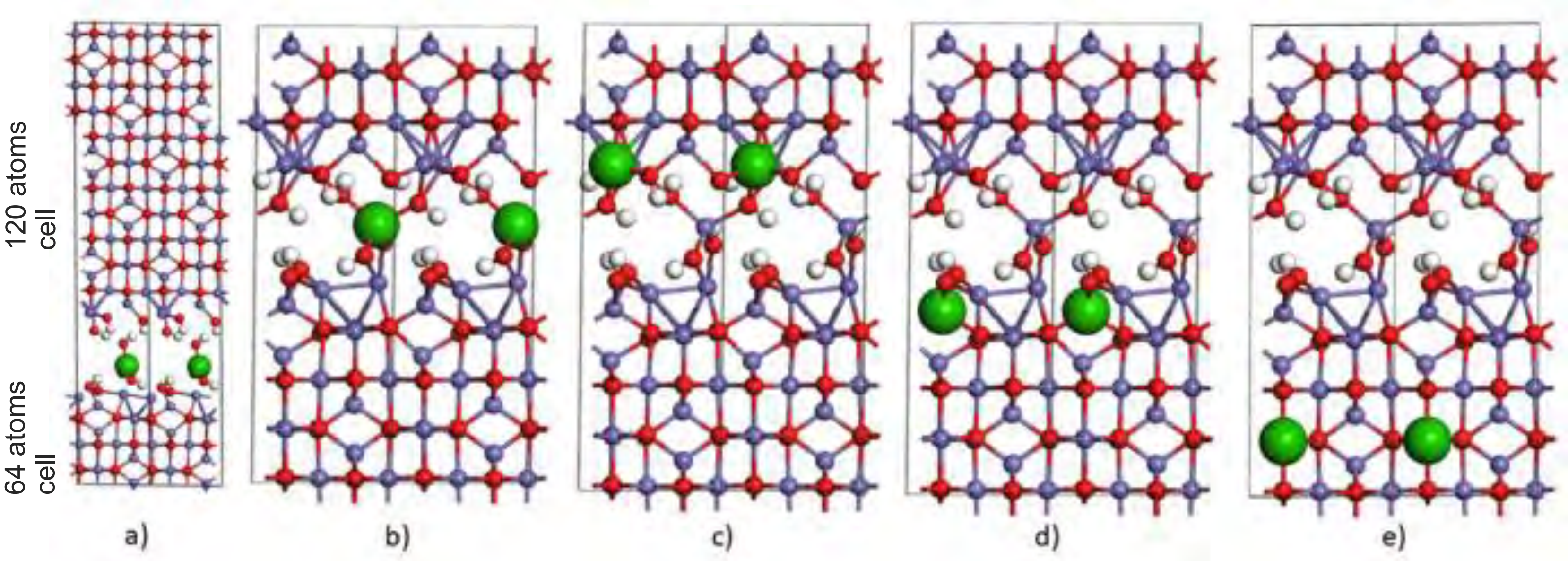


Acronyms





$M(OH)_2@(W/O)$



M^{2+} in coolant

Supercell

HGBI
Hydroxylated grain boundary ion

M^{2+}@(OOS)
M^{2+} at outer octahedral site

M^{2+}@(OTS)
M^{2+} at outer tetrahedral site

M^{2+}@(IOS)
M^{2+} at inner octahedral site

Hypothesis

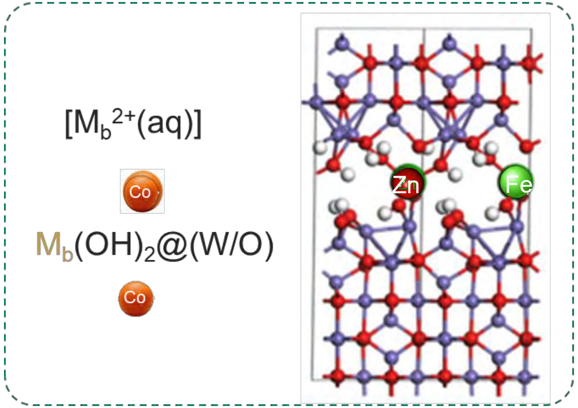
Pathway for $Co^{2+}_{(aq)}$ deposition

1	$Co(OH)_2$@(W/O) + $Fe(OH)_2$@(HGBI) → $Fe(OH)_2$ + $Co(OH)_2$@(HGBI) Co^{2+} in coolant migrates to become hydroxylated grain boundary Co ion
2	$Co(OH)_2$@(HGBI) → (H_2O)CoO@(GB) Hydroxylated grain boundary Co ion attaches to GB and the protons to form H_2O
3	(H_2O)CoO@(GB) + Fe^{2+}@(OOS) → (H_2O)FeO@(GB) + Co^{2+}@(OOS) Co@GB exchanges with Fe^{2+}@OOS
4	Co^{2+}@(OOS) + Fe^{2+}@(IOS) → Fe^{2+}@(OOS) + Co^{2+}@(IOS) Co^{2+}@(OOS) moves inward to become Co^{2+}@(IOS)

Step 1

To become the hydroxylated GB ions

M^{2+} - Fe^{2+}	ΔG ~ ΔH (eV)
Ni^{2+} - Fe^{2+}	0.05
Co^{2+} - Fe^{2+}	-0.26
Zn^{2+} - Fe^{2+}	-0.79
Zn^{2+} - Ni^{2+}	-0.84
Zn^{2+} - Co^{2+}	-0.53
Co^{2+} - Ni^{2+}	-0.31



[1] $Co(OH)_2$@(W/O) + $Fe(OH)_2$@(HGBI) → $Fe(OH)_2$ + $Co(OH)_2$@(HGBI)

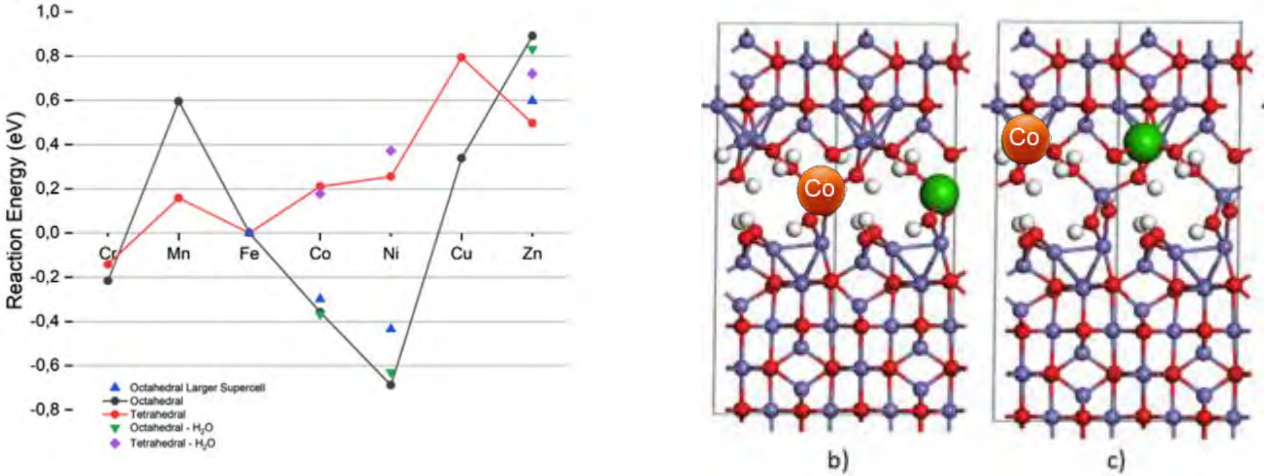
[2] $Co(OH)_2$@(HGBI) → $(H_2O)CoO$@(GB)

[3] $(H_2O)CoO$@(GB) + Fe^{2+}@(OOS) → $(H_2O)FeO$@(GB) + Co^{2+}@(OOS)

[4] Co^{2+}@(OOS) + Fe^{2+}@(IOS) → Fe^{2+}@(OOS) + Co^{2+}@(IOS)

Steps 2-3

To become accommodated at spinel (OOS)/(OTS) sites (1)



[1] $Co(OH)_2$@(W/O) + $Fe(OH)_2$@(HGBI) → $Fe(OH)_2$ + $Co(OH)_2$@(HGBI)

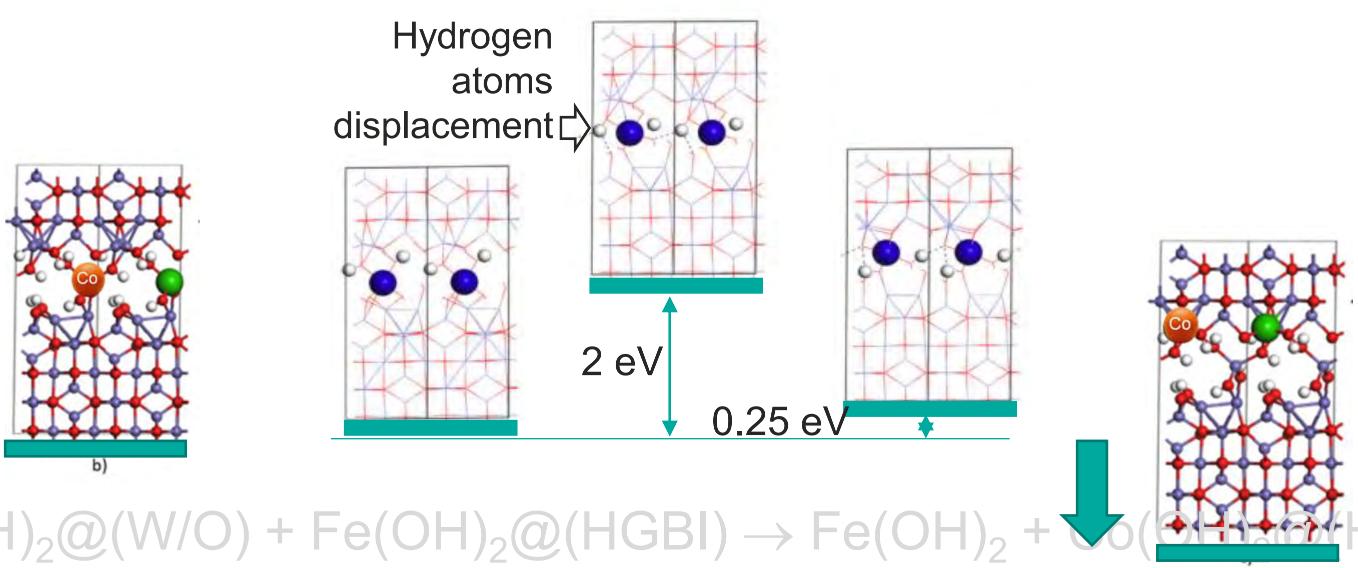
[2] $Co(OH)_2$@(HGBI) → $(H_2O)CoO$@(GB)

[3] $(H_2O)CoO$@(GB) + Fe^{2+}@(OOS) → $(H_2O)FeO$@(GB) + Co^{2+}@(OOS)

[4] Co^{2+}@(OOS) + Fe^{2+}@(IOS) → Fe^{2+}@(OOS) + Co^{2+}@(IOS)

Steps 2-3

To become accommodated at spinel (OOS)/(OTS) sites (2)



[1] $Co(OH)_2@(W/O) + Fe(OH)_2@(HGBI) \rightarrow Fe(OH)_2 + Co(OH)_2@(HGBI)$

[2] $Co(OH)_2@(HGBI) \rightarrow (H_2O)CoO@(GB)$ **+2 eV**

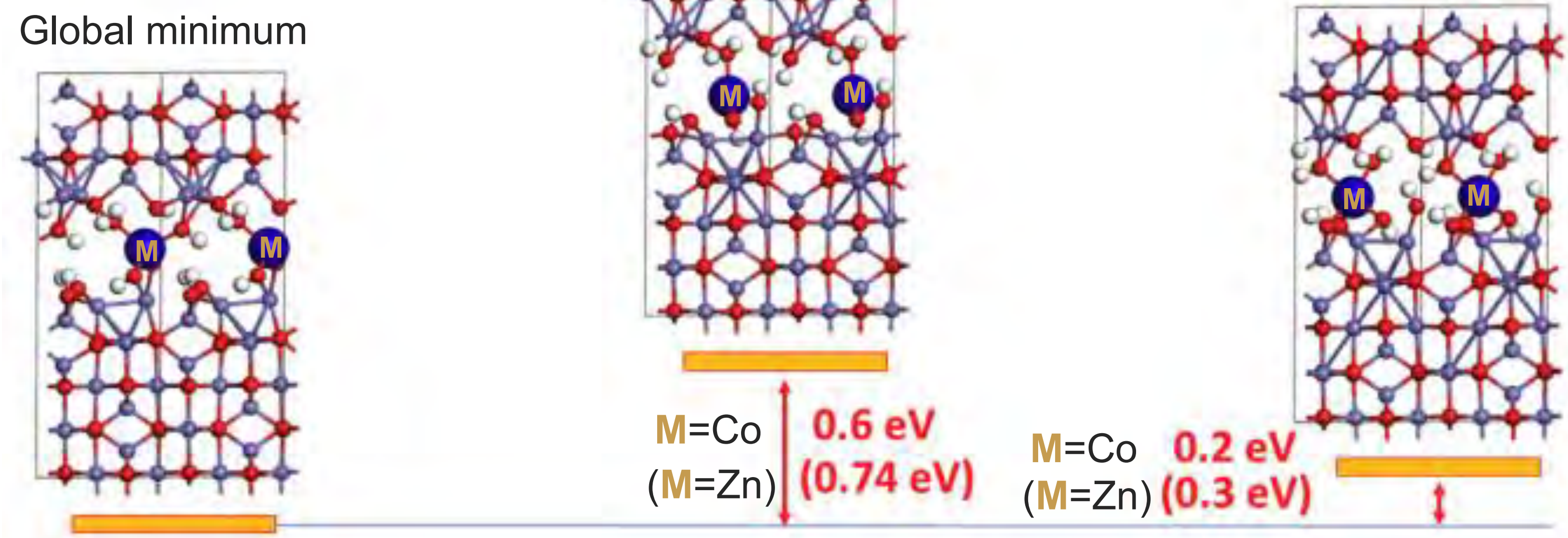
[3] $(H_2O)CoO@(GB) + Fe^{2+}@(OOS) \rightarrow (H_2O)FeO@(GB) + Co^{2+}@(OOS)$ **-0.56 eV**

[4] $Co^{2+}@(OOS) + Fe^{2+}@(IOS) \rightarrow Fe^{2+}@(OOS) + Co^{2+}@(IOS)$

Mobility @(HGBI) for Co and Zn

E_a=1 eV

(measured for Co)



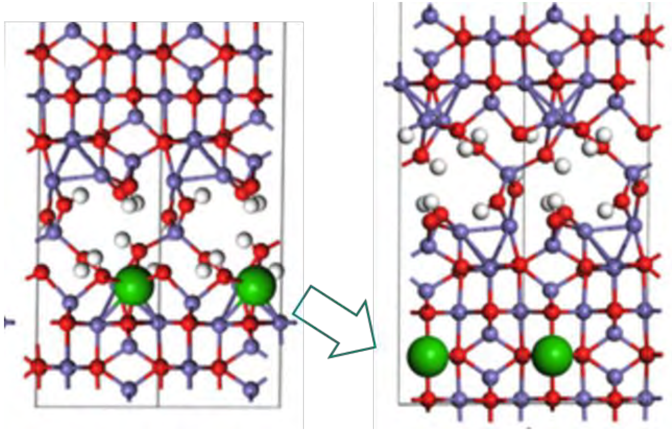
Step 4: Essential for accommodating more Co^{2+} in spinel

Co^{2+}@(OOS) → Co^{2+}@(IOS)

[Fe_3O_4] $Co^{2+} \leftrightarrow Fe^{2+}$ ΔH=0.4 eV

[$NiFe_2O_4$] $Co^{2+} \leftrightarrow Ni^{2+}$ ΔH=-0.18 eV

Co-60 uptake is enhanced in $NiFe_2O_4$ as compared to Fe_3O_4



[1] $Co(OH)_2$@(W/O) + $Fe(OH)_2$@(HGBI) → $Fe(OH)_2$ + $Co(OH)_2$@(HGBI)

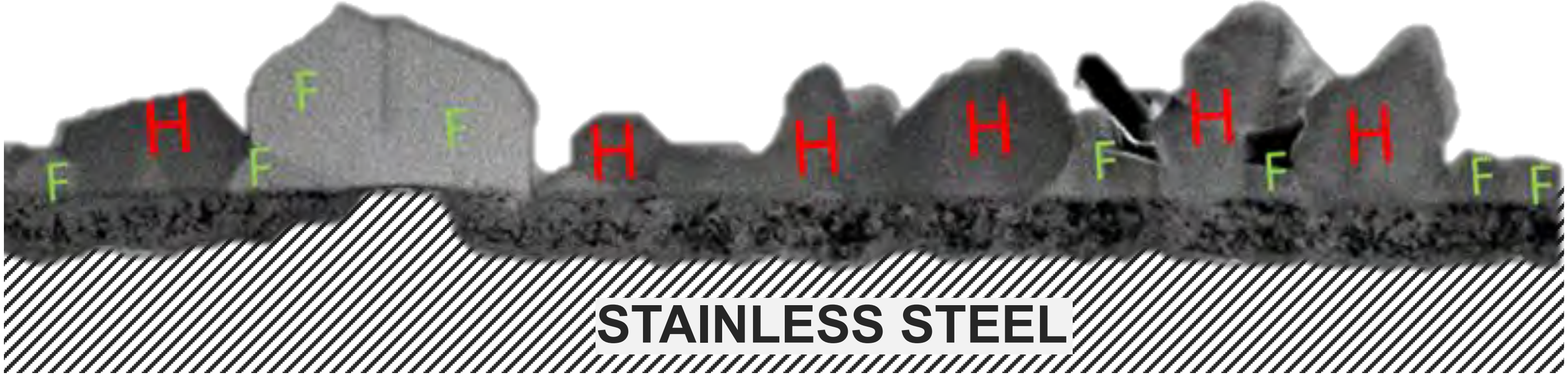
[2] $Co(OH)_2$@(HGBI) → (H_2O)CoO@(GB) +2 eV

[3] (H_2O)CoO@(GB) + Fe^{2+}@(OOS) → (H_2O)FeO@(GB) + Co^{2+}@(OOS) -0.56 eV

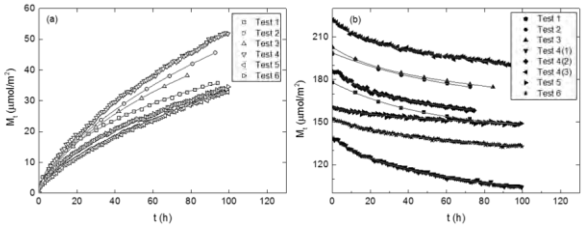
[4] Co^{2+}@(OOS) + Fe^{2+}@(IOS) → Fe^{2+}@(OOS) + Co^{2+}@(IOS)

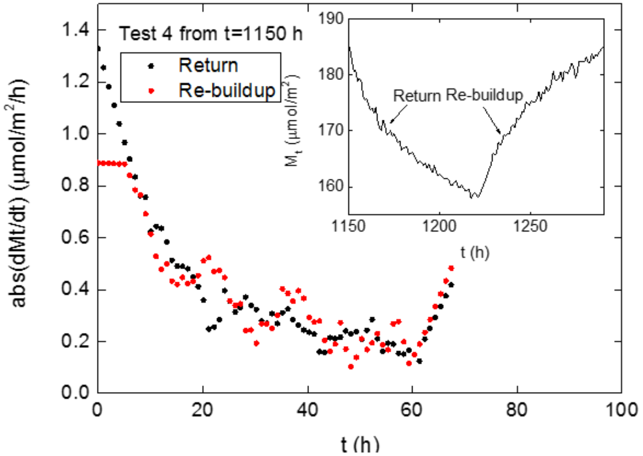
Co deposition in real life…

- *On outer ferrite grain surfaces*
  - Reprecipitation > surface diffusion > adsorption > inward diffusion
- *In porous inner spinel layer*
  - Interchange reaction > interface diffusion > adsorption > inward diffusion

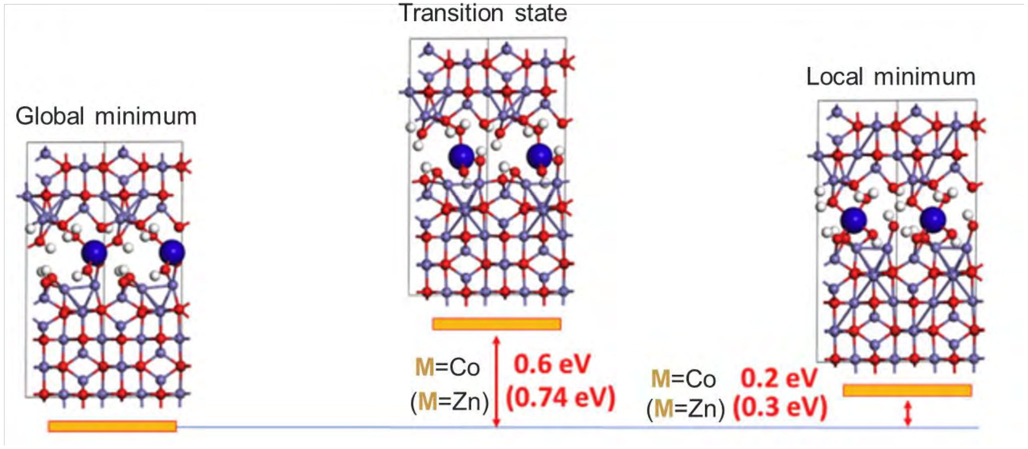


The reversible Co deposition and release (step 1)

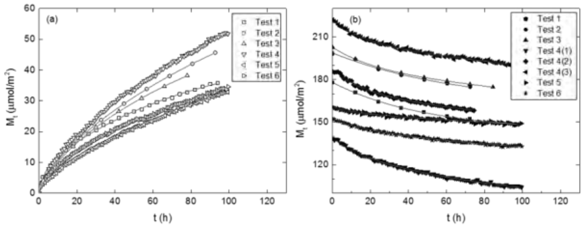


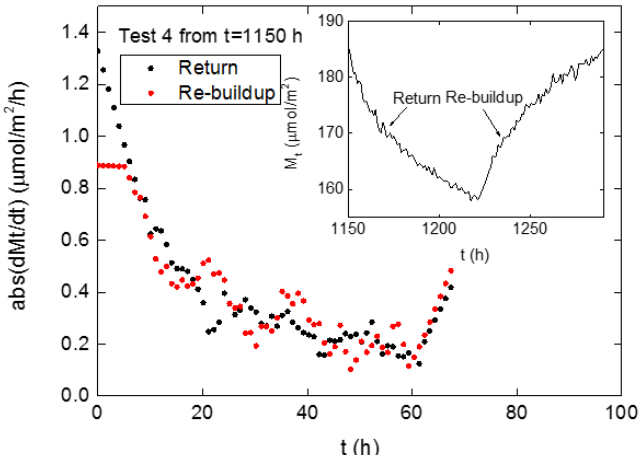


In pure coolant with a fresh oxide film, Co^{2+} diffusion into the interface (drive: Co^{2+} activity difference)



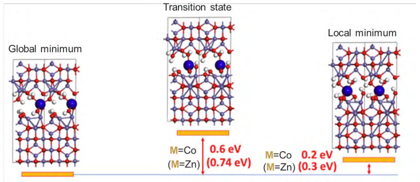
The reversible Co deposition and release (steps 2-3)

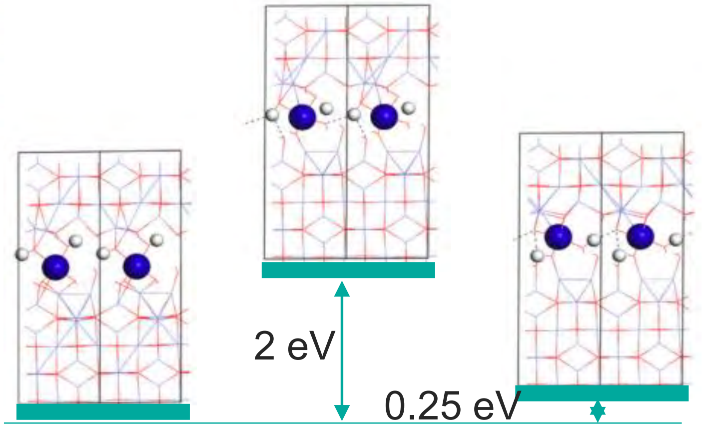




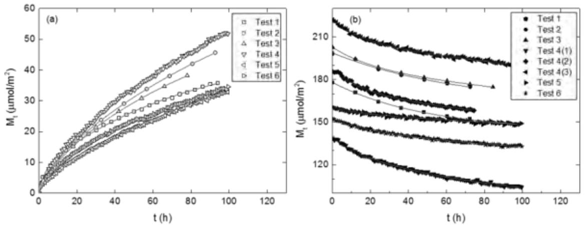
To further move to OOS site via the transition state costs a large energy: Co$(OH)_2$@(HGBI) → (H_2O)CoO@(GB) +2 eV

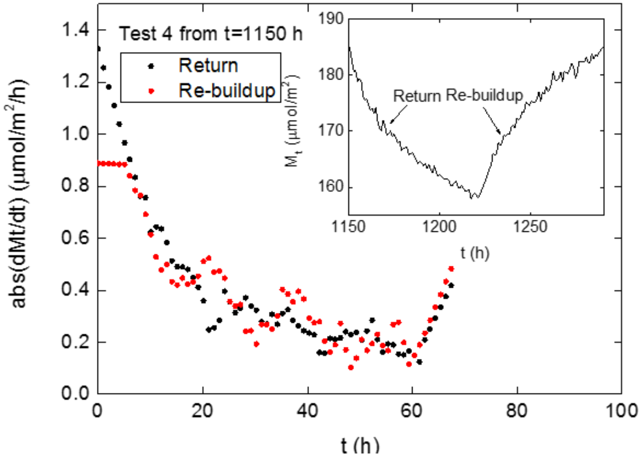
Co^{2+} moving out from (OOS) site in reverse direction would be a difficult path!



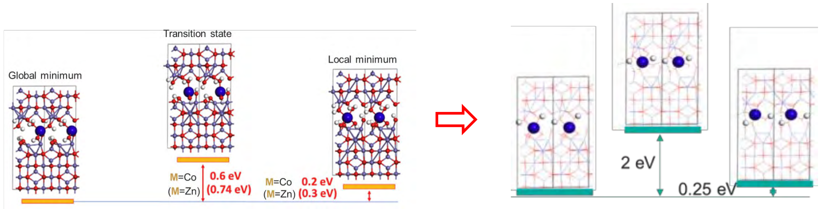


The reversible Co deposition and release (step 4)





Once got into (OOS) sites, further absorption into lattice is easy in $NiFe_2O_4$ but not so easy in Fe_3O_4



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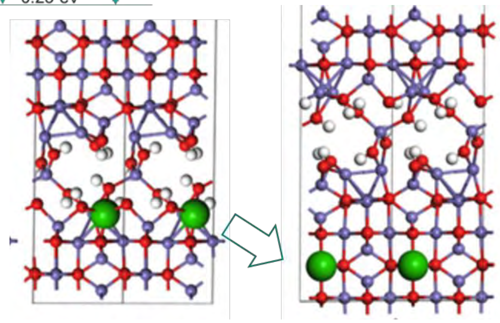
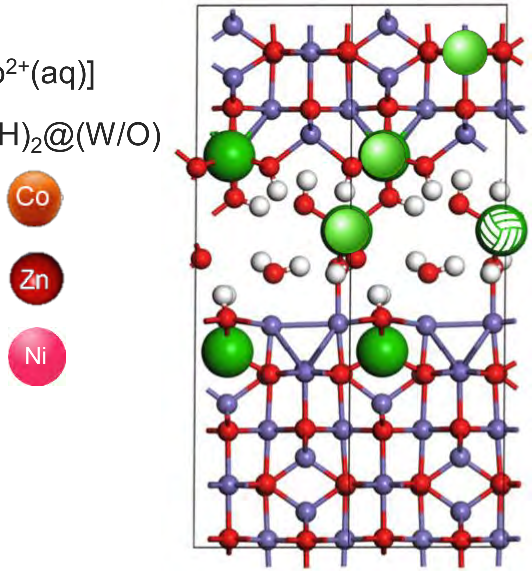


Summary

How do $Co^{2+}_{(aq)}$ deposit?

[Co^{2+}(aq)]

$Co(OH)_2$@(W/O)

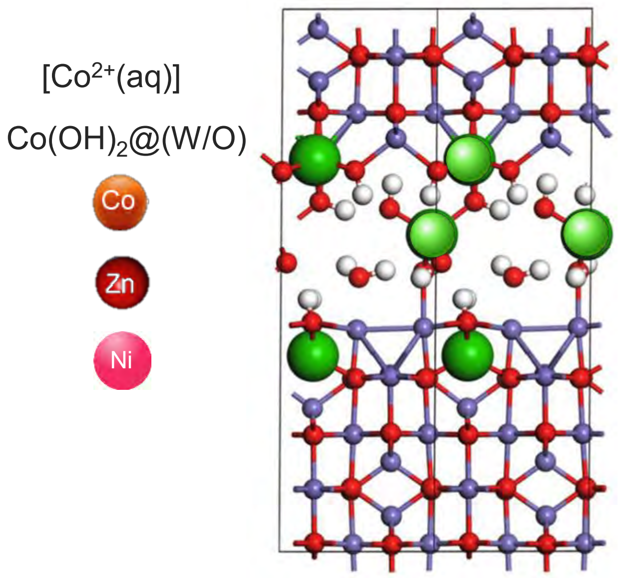


Co^{2+}(aq)

Reaction	
$Co(OH)_2$@(W/O) + $Fe(OH)_2$@(HGBI) → $Fe(OH)_2$ + $Co(OH)_2$@(HGBI)	R1
$Co(OH)_2$@(HGBI) → (H_2O)CoO@(GB)	R2
(H_2O)CoO@(GB) + Fe@(OOS) → (H_2O)FeO@(GB) + Co^{2+}@(OOS)	R3
Co^{2+}@(OOS) + Fe^{2+}@(IOS) → Fe^{2+}@(OOS) + Co^{2+}@(IOS)	R4

Summary

How do $Zn^{2+}_{(aq)}$ suppress Co-uptake?



- $Zn(OH)_2$@(W/O)+$Fe(OH)_2$@(HGBI) → $Fe(OH)_2$@(W/O) +$Zn(OH)_2$@(HGBI)
- E_a of $Zn(OH)_2$@(HGBI) is 0.74 eV
- $Zn(OH)_2$@(HGBI) blocks $Co(OH)_2$@(HGBI)
- Zn^{2+} in coolant blocks Co^{2+} reprecipitation (forming outer oxide grains)

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