"IN-SITU" SPECTRO-ELECTROCHEMICAL STUDIES OF RADIONUCLIDE CONTAMINATED SURFACE FILMS ON METALS*

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ABSTRACT

The incorporation of Sr, Ce, and Cr into nickel hydrous oxide films has been studied using “in-situ” X-ray Absorption Spectroscopy (XAS) and electrochemical techniques. Sr (II) and Ce (III, IV) hydrous oxides were found to co-precipitate and form separate phase domains. Cr (III) occupies Ni vacancy sites, while Cr (VI) was found in the interlamellar position in the $Ni(OH)_2$ films. Bond distances and co-ordination numbers have been obtained.

FOCUS AREA

DECONTAMINATION AND DECOMMISSIONING

NEED BEING ADDRESSED

DECONTAMINATION OF STORAGE TANKS,

PIPING SYSTEMS, AND METAL SURFACES

IN NUCLEAR FACILITIES

TECHNICAL APPROACH

- radioactive contamination resides in corrosion scales and surface films
- corrosion is essentially an electrochemical process

- simulate film formation via electrochemical deposition
- study incorporation of heavy metal ions and radionuclides in the film by "in situ" spectroscopic techniques, i.e., synchrotron X-ray absorption (XAS) and vibrational (laser Raman, infrared) spectroscopy

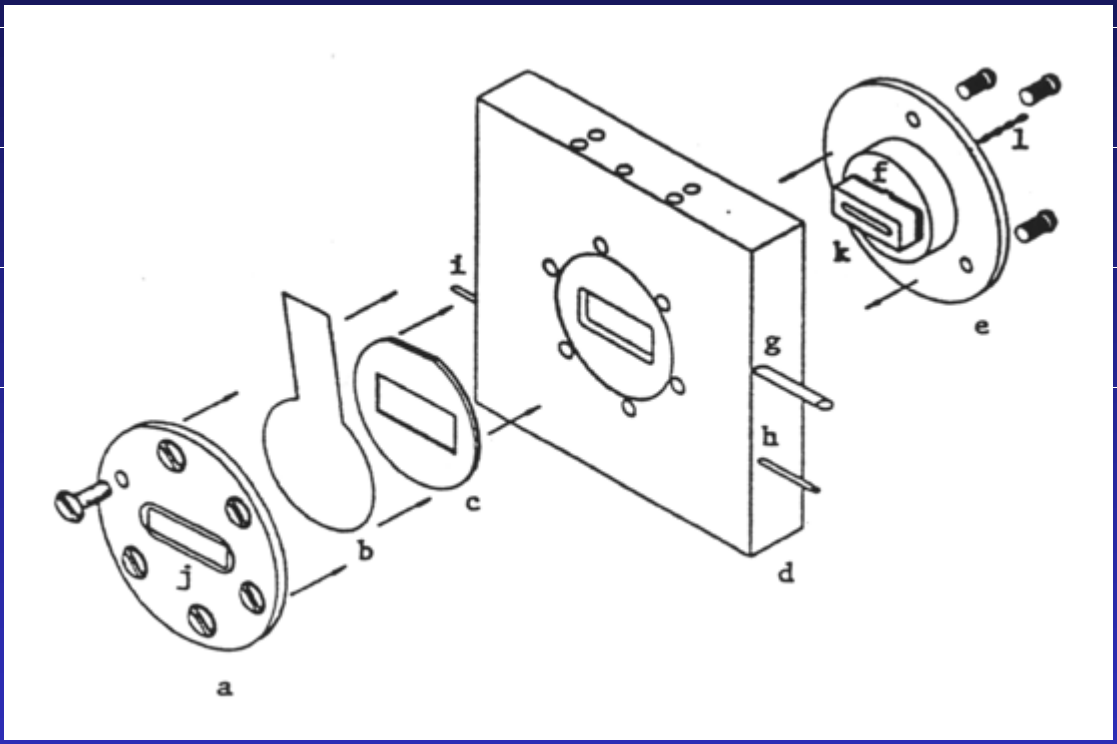
- use the basic knowledge gained to develop decontamination, decommissioning, and disposal technologies

RESEARCH PLAN

- corrosion films of base metals Fe, Ni, Cr, and Steel
- radioactive contaminants-Sr, Cs, Ce, U, Pu
- pH (1-14), ion concentration, T (25 to 95 degrees C)

EXPERIMENTAL

XAS-Electrochemical Cell



b- graphite working electrode
f- gold counter electrode
i- reference electrode (SCE)

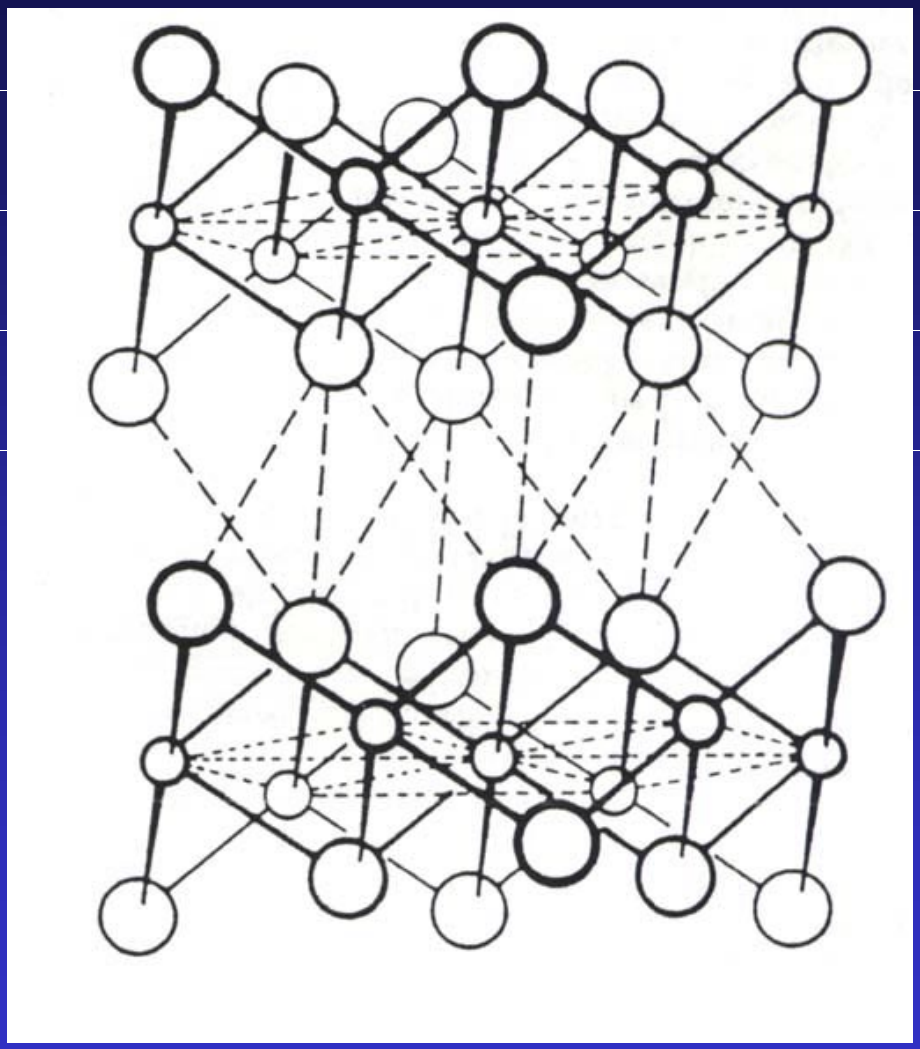
Procedure

- Cathodic co-deposition of $Ni(OH)_2$ + Me^{+z}
  - 0.1 M $Ni(NO_3)_2$ + 0.0005 to 0.1 M Me^{+z} salt solutions, pH= 5.1
  - current density = -5 to -20 mA/cm^2

- Anodic co-deposition of NiOOH + Me^{+z}
  - 0.05 M $NiSO_4$ + 0.5 M Na_2SO_4 + 0.0005 to 0.1 M Me^{+z} salt solution, pH= 7.4
  - applied potential =1.1 V vs SCE

RESULTS

STRUCTURE OF $Ni(OH)_2$



OH

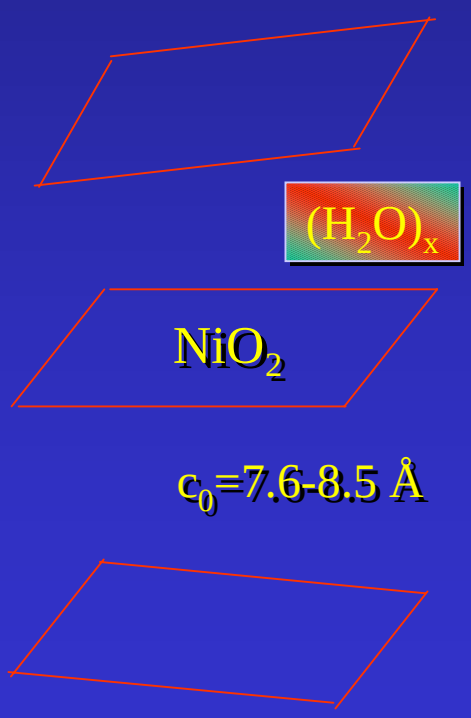
Ni

Brucite structure--- $Ni(OH)_2$ layers

STRUCTURE OF ELECTRODEPOSITED NICKEL OXIDES

α - $Ni(OH)_2$

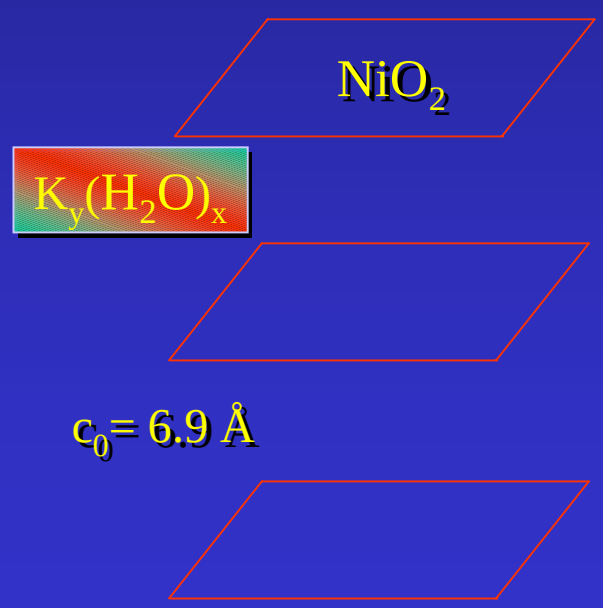
a_0=3.05 Å



c_0=7.6-8.5 Å

γ-NiOOH

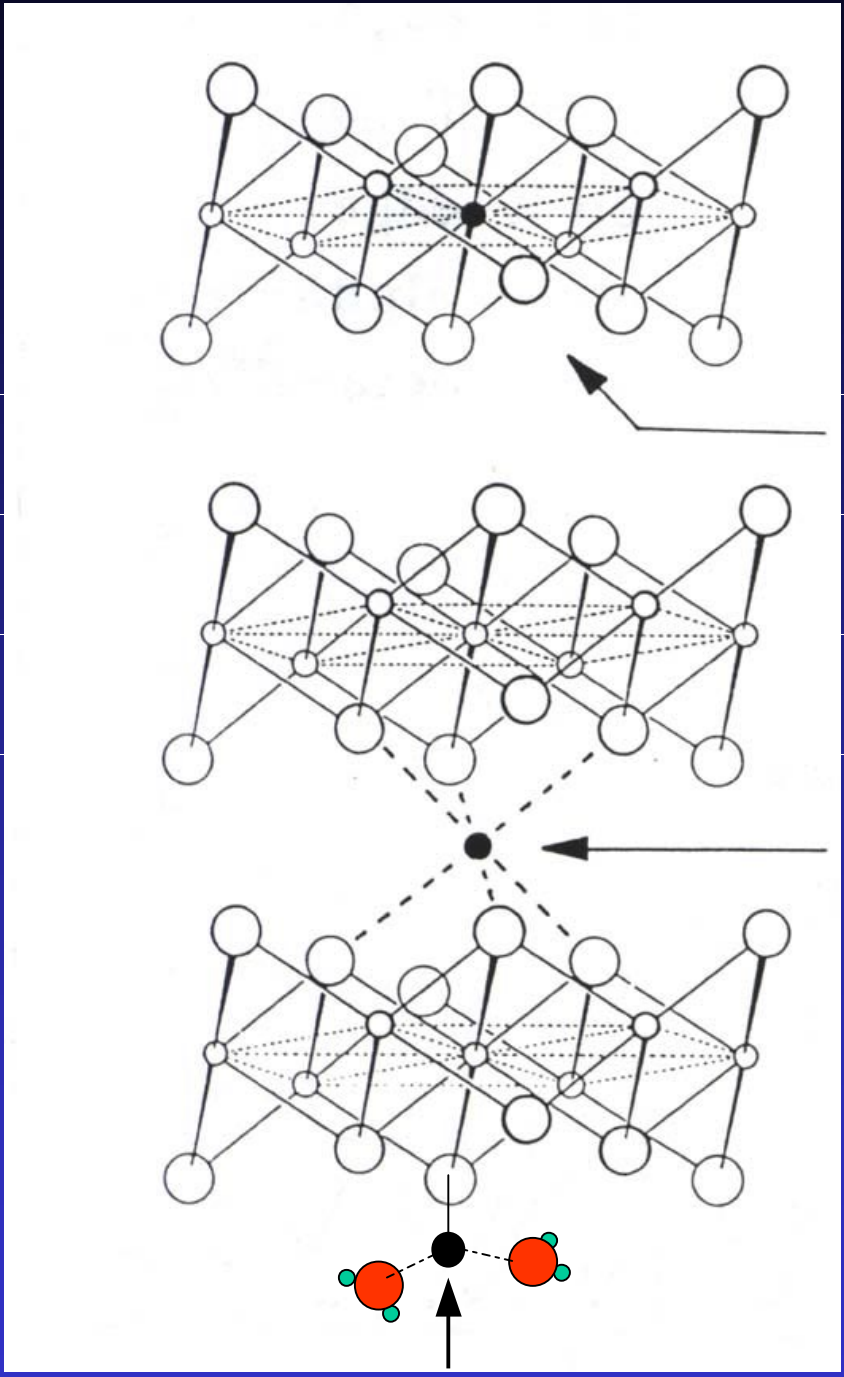
a_0=2.82 Å



c_0= 6.9 Å

MECHANISMS and SITES for INCORPORATION

- surface adsorption
- lattice sites (vacancies) -Cr (III)
- interlamellar positions - Cr (VI)
- co-precipitation and deposition in separate phase domains - Sr (II), Ce (III, IV)
- absorption in pores


Lattice site
Interlamellar site
Surface site

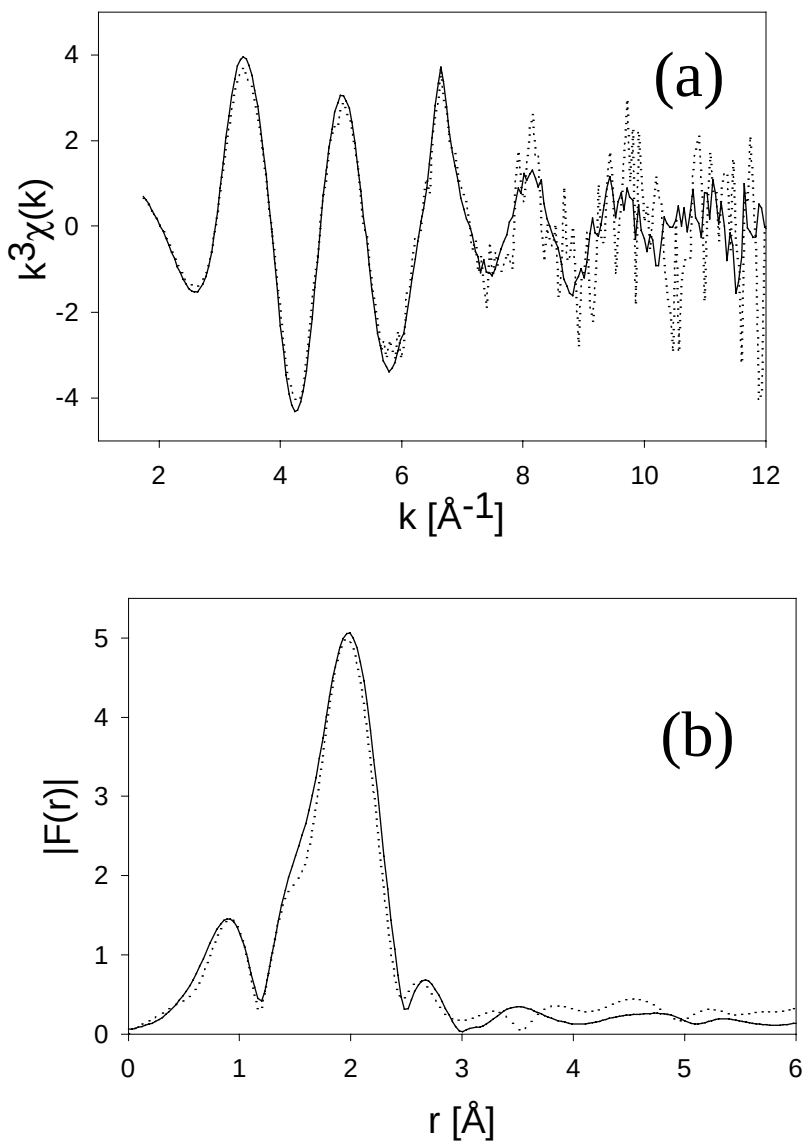
STRONTIUM

• See only Sr-O bonds for Sr (II) in $Ni(OH)_2$ and NiOOH from EXAFS data down to 12 K, Sr (II) concentration = 0.0005 to 0.1 M

• Sr-O distance = 2.62 Å, similar to Sr (II) in solution and pure $Sr(OH)_2$ cathodically deposited

• Coordination number, N~ 8-10

•Co-precipitation and formation of separate domains are suggested; extent of surface adsorption not delineated so far



(a) Sr K-edge EXAFS for Sr^{2+} in α-$Ni(OH)_2$ (dotted) and in 0.1 M Sr-acetate solution (solid)

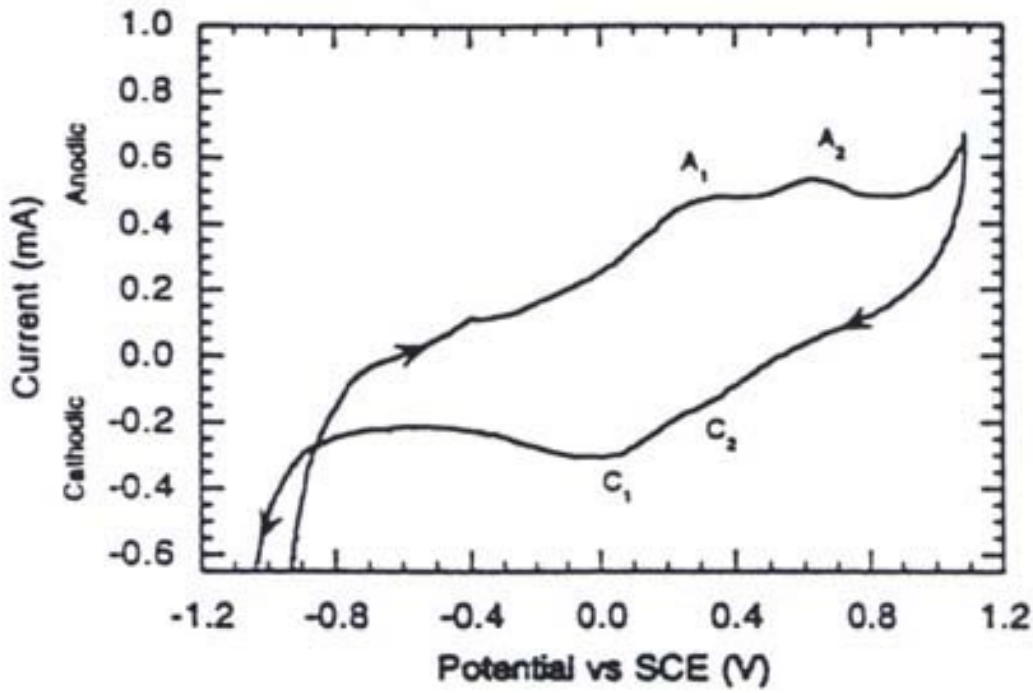
(b) Corresponding k^3-weighted Fourier transform

CERIUM

- Found mixed Ce (III) and Ce (IV) phases co-deposited with $Ni(OH)_2$

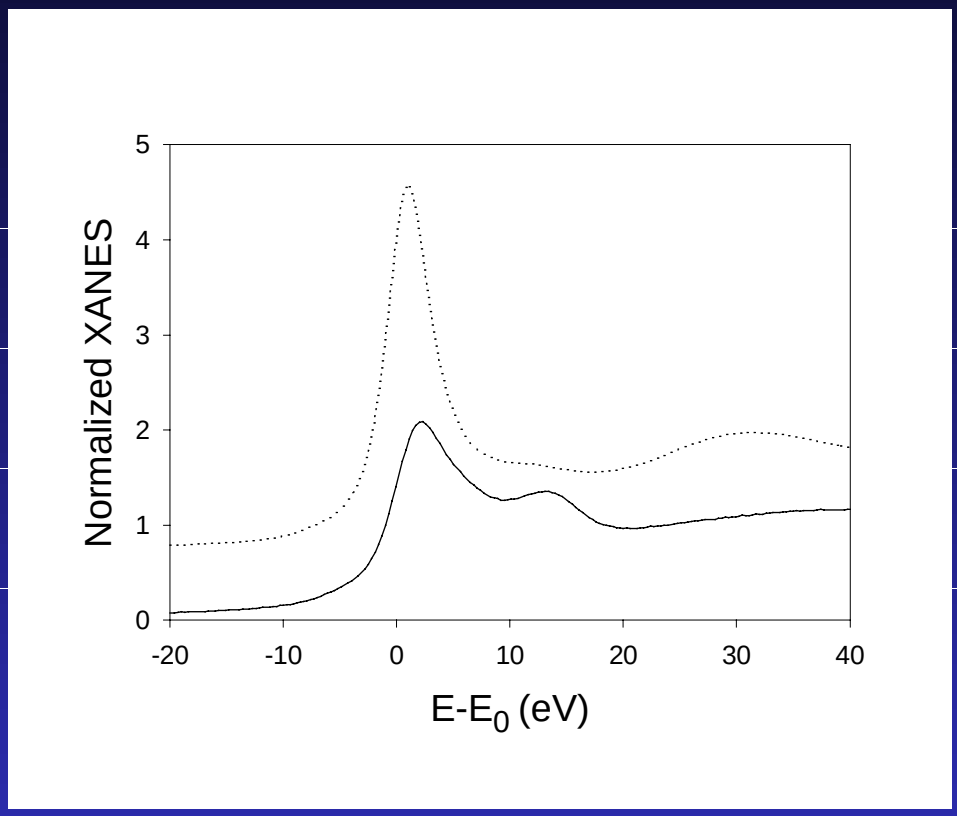
- Only Ce (IV) found with NiOOH; phase corresponds to hydrous CeO_2

- Determined Ce-Ce bond distances and coordination numbers from analysis of EXAFS data

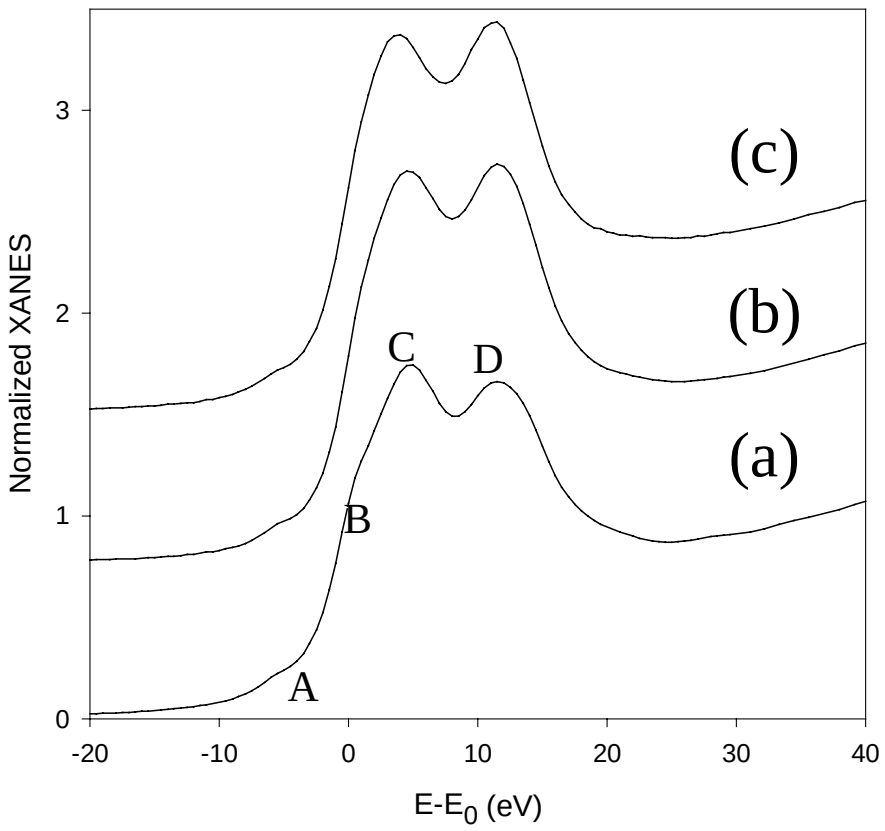


Cyclic voltammogram at a graphite electrode

* 0.04 M Ce (III) acetate + 0.05 M $NiSO_4$ + 0.5 M Na acetate solution
* scan rate = 10 mv/sec



XANES of Ce co-deposited with $Ni(OH)_2$ film (solid) and spectrum of 0.08 M Ce (III) acetate solution (dotted)



Ce-L_3 edge XANES spectra

(a) CeO_2

(b) $Ce(OH)_4$

(c) Ce co-deposited with NiOOH

CHROMIUM

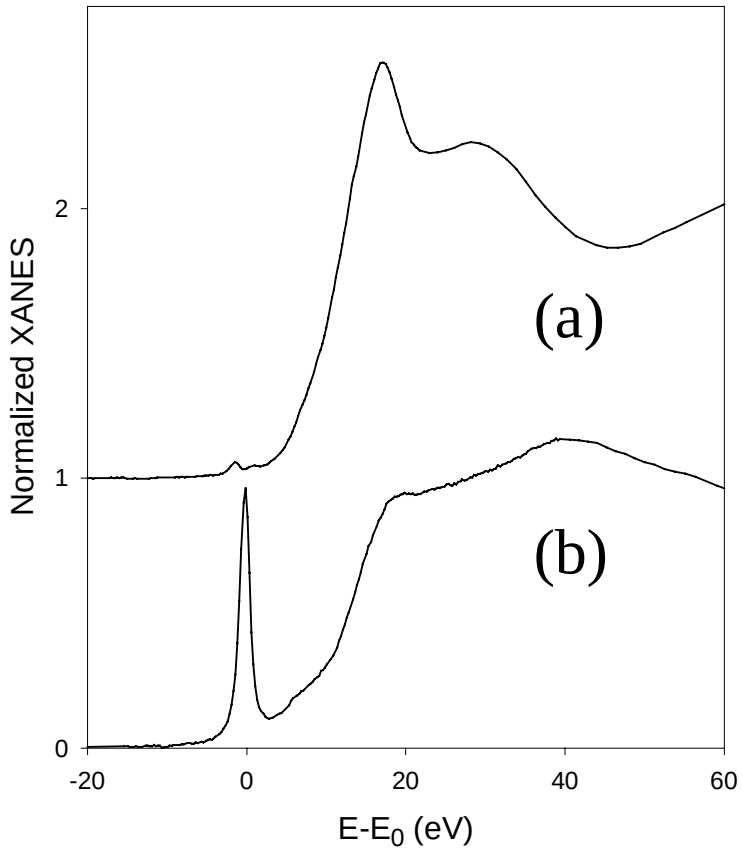
- Co-deposition of Cr(III) with $Ni(OH)_2$ results in Cr(III) in lattice sites substituting for Ni (II)

  *Bond distances found: Cr-O = 1.99 Å (N=6), Cr-Ni = 3.09 Å (N=6)

- Co- deposition from CrO_4^{2-} solution yields Cr (VI) in interlamellar positions

  *Cr-O distance = 1.66 Å, N=4, as in CrO_4^{2-}

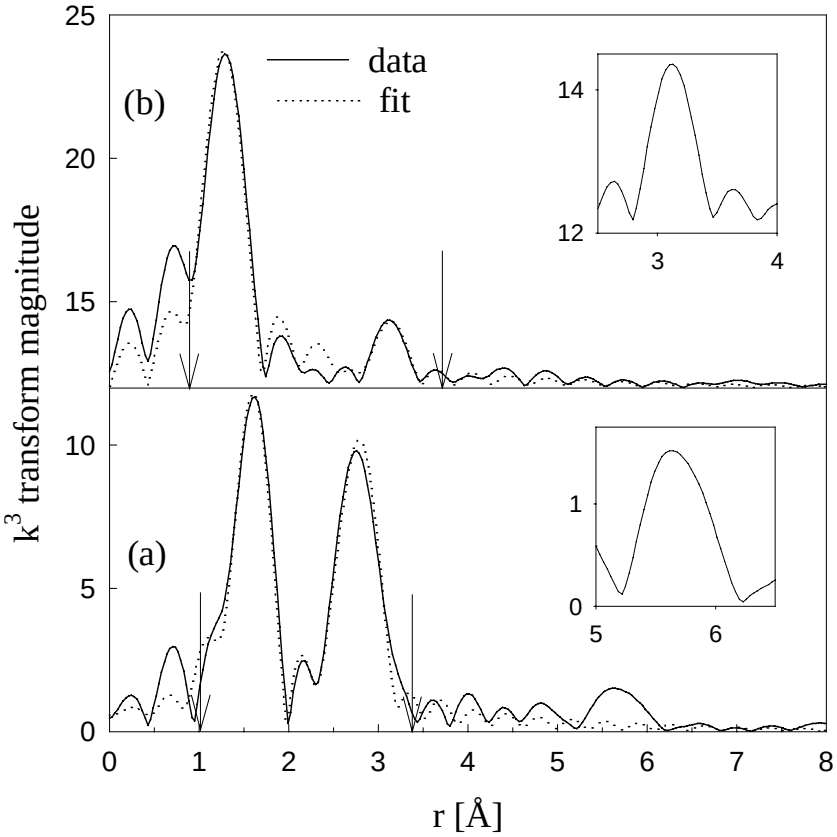
  *Cr-Ni distance = 3.41 Å, N=2



Cr K-edge XANES

(a) Cr (III) in $Ni(OH)_2$

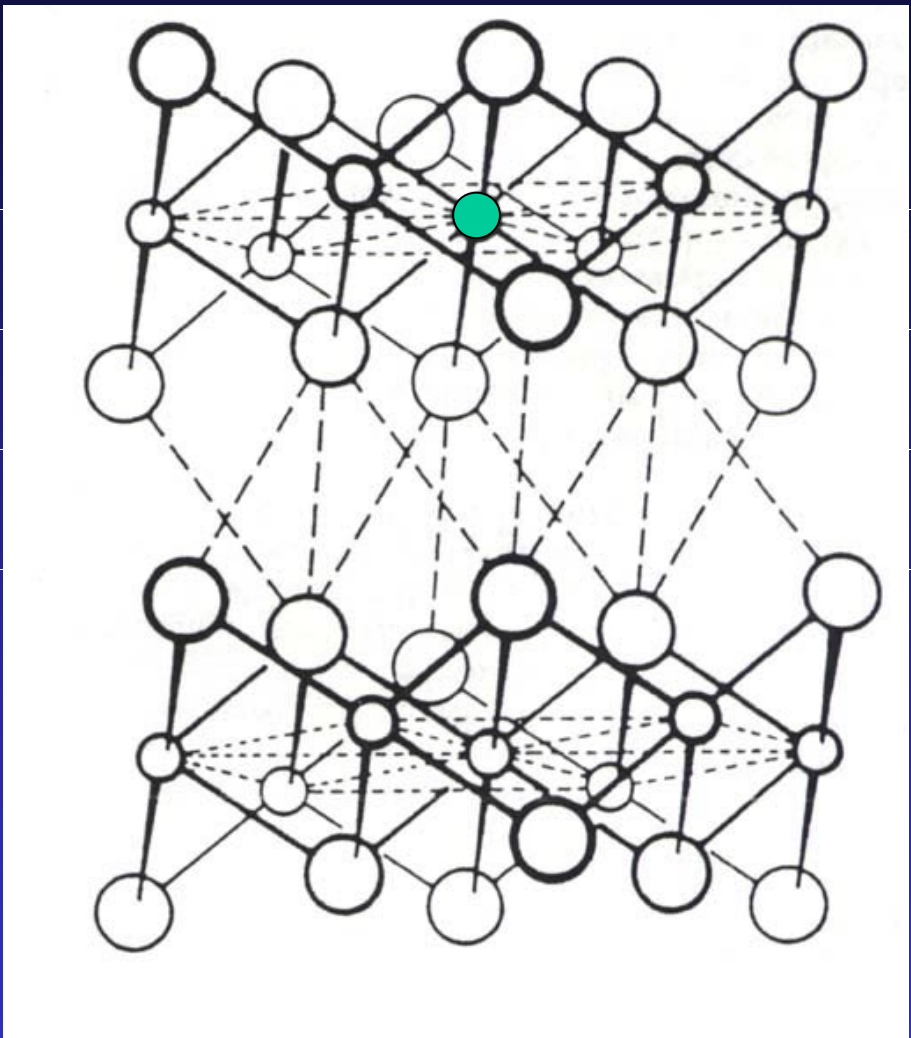
(b) Cr (VI) in $Ni(OH)_2$



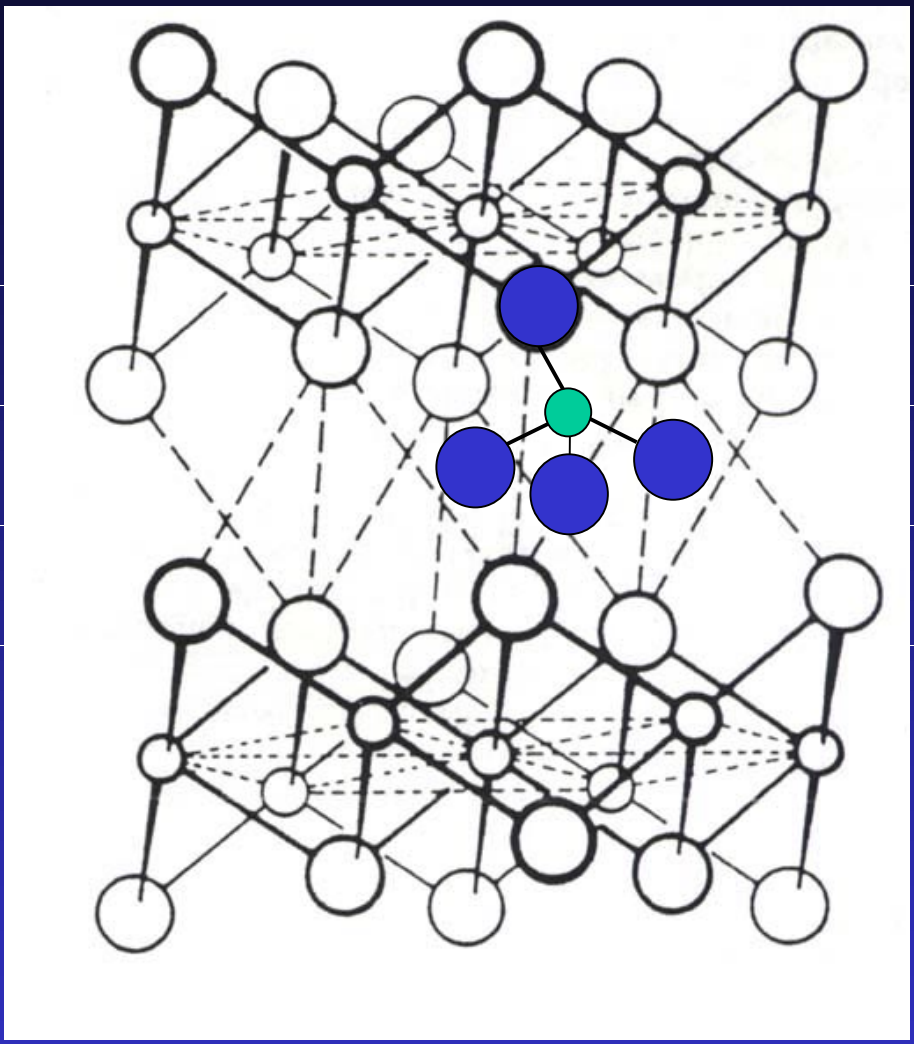
Fourier transform (k^3-weighted) of Cr K-edge EXAFS

(a) Cr (III) incorporated into α-$Ni(OH)_2$

(b) Cr (VI) incorporated into α-$Ni(OH)_2$



Cr^{3+} ------> Ni lattice sites



Cr^{6+} -----> Interlamellar sites

CONCLUSIONS

Scientific significance:

* Demonstrated the utility of XAS for determining “in situ” the mode of incorporation and local structure of metal ion contaminants in thin, disordered simulated corrosion films.

* Bonding configuration dependent on size and charge of ion, structure of host oxide, solution composition, pH, etc.

Practical relevance:

- Knowledge of binding site will be useful in designing decontamination procedures

  - surface-adsorbed contaminant -----> “mild treatment”, e.g., oxalic acid contacting

  - ions in lattice sites -----> “aggressive treatment” with complete dissolution of corrosion scale, e.g., electropolishing in hot phosphoric acid

  - co-precipitates -----> selectively dissolve

FUTURE WORK

- Study the effect of radiation on the structure and mechanism of incorporation of contaminant metal ion into corrosion films

- Investigation at pH < 4, ion concentration < 0.0005 M, 25 < T < 95 degrees C

Acknowledgements

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