Química Analítica II: Separación de Ni (II) y Cd(II) a pH impuesto

Estudio gráfico.

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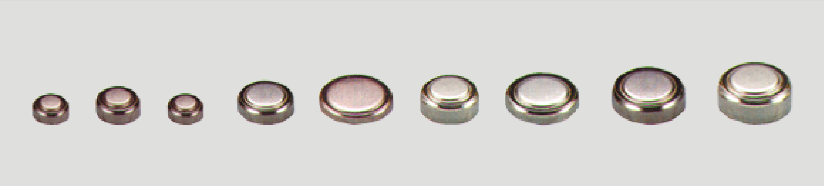
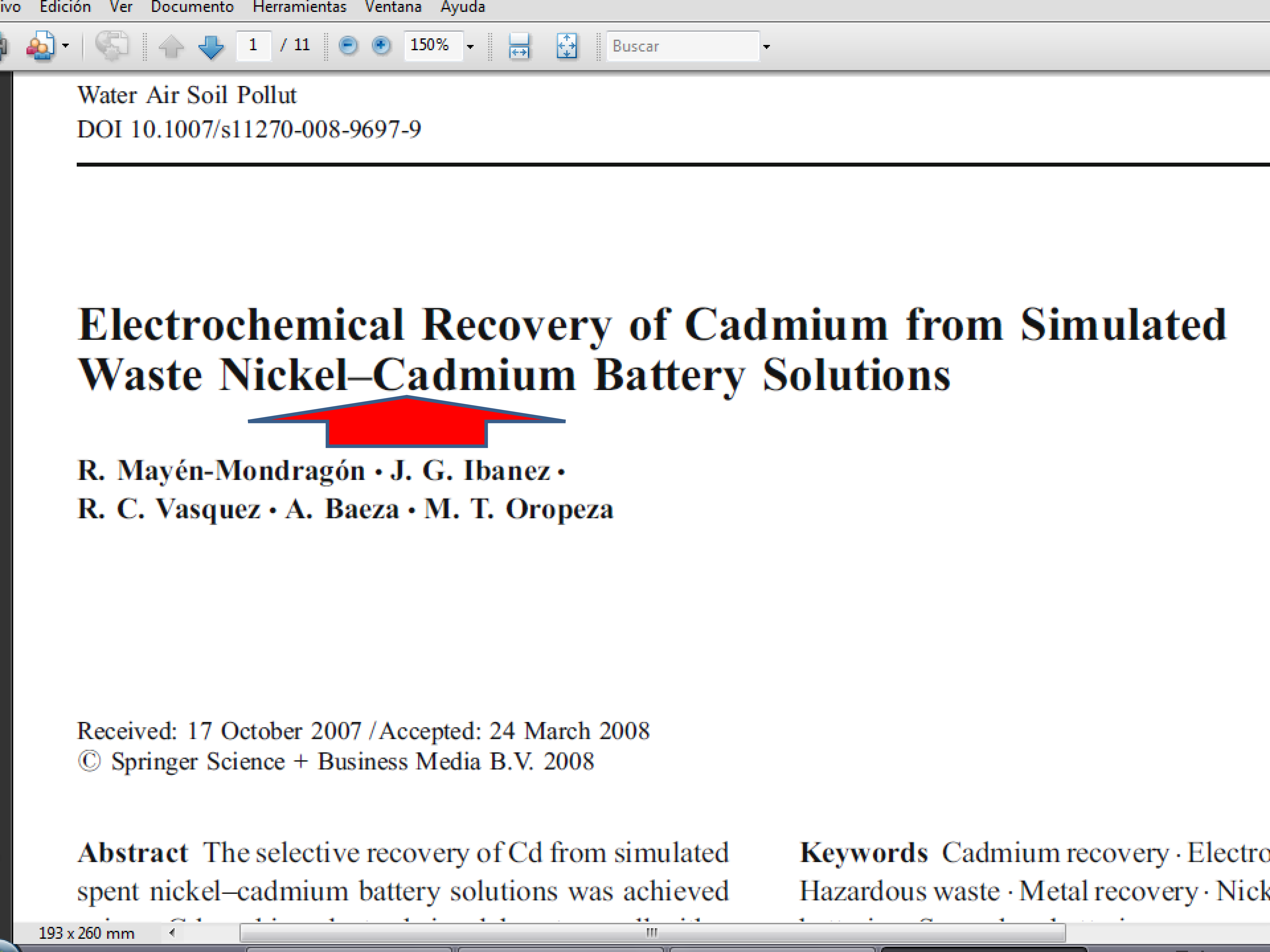
¿Porqué separar Ni(II) y Cd(II)?:

Nano, coche del futuro:

La electricidad se almacena en 19 baterías de níquel-cadmio cuya vida estimada es de 10 años, su recarga se puede realizar directamente desde una toma de corriente doméstica de 220V, necesita de 8 horas para tener una recarga completa y 5 horas para recargar el 80%. Puede conseguir una velocidad máxima de 100 km/h, llega a 50 km/h en 7 segundos y supera pendientes del 30% (un Pontiac Matiz de 65 HP sube pendientes de 40%) lo que lo limita para su uso exclusivo en ciudad.





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Electrochemical Recovery of Cadmium from Simulated Waste Nickel–Cadmium Battery Solutions

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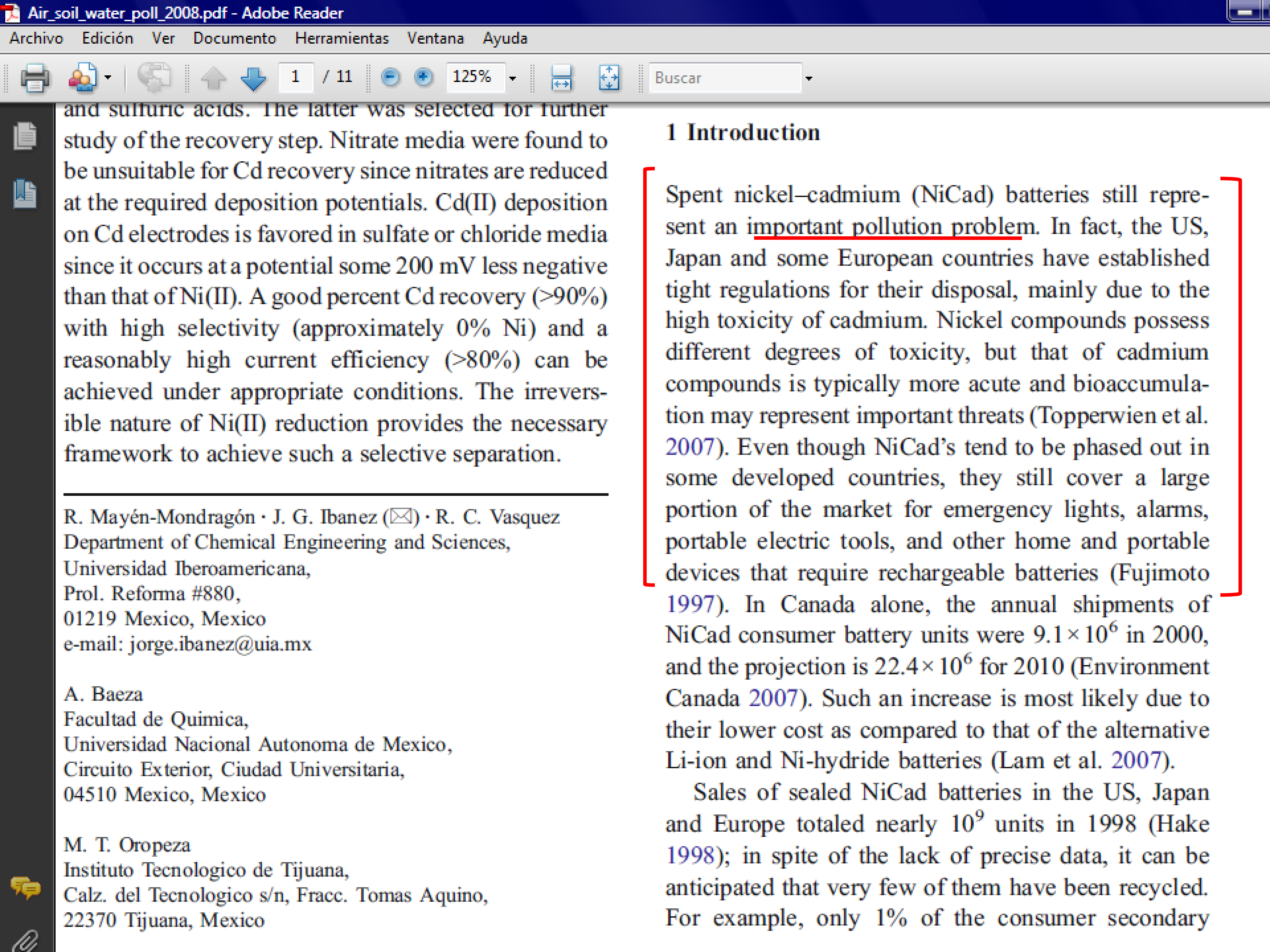
Abstract The selective recovery of Cd from simulated spent nickel–cadmium battery solutions was achieved

Keywords Cadmium recovery · Electro
Hazardous waste · Metal recovery · Nick



and sulfuric acids. The latter was selected for further study of the recovery step. Nitrate media were found to be unsuitable for Cd recovery since nitrates are reduced at the required deposition potentials. Cd(II) deposition on Cd electrodes is favored in sulfate or chloride media since it occurs at a potential some 200 mV less negative than that of Ni(II). A good percent Cd recovery (>90%) with high selectivity (approximately 0% Ni) and a reasonably high current efficiency (>80%) can be achieved under appropriate conditions. The irreversible nature of Ni(II) reduction provides the necessary framework to achieve such a selective separation.

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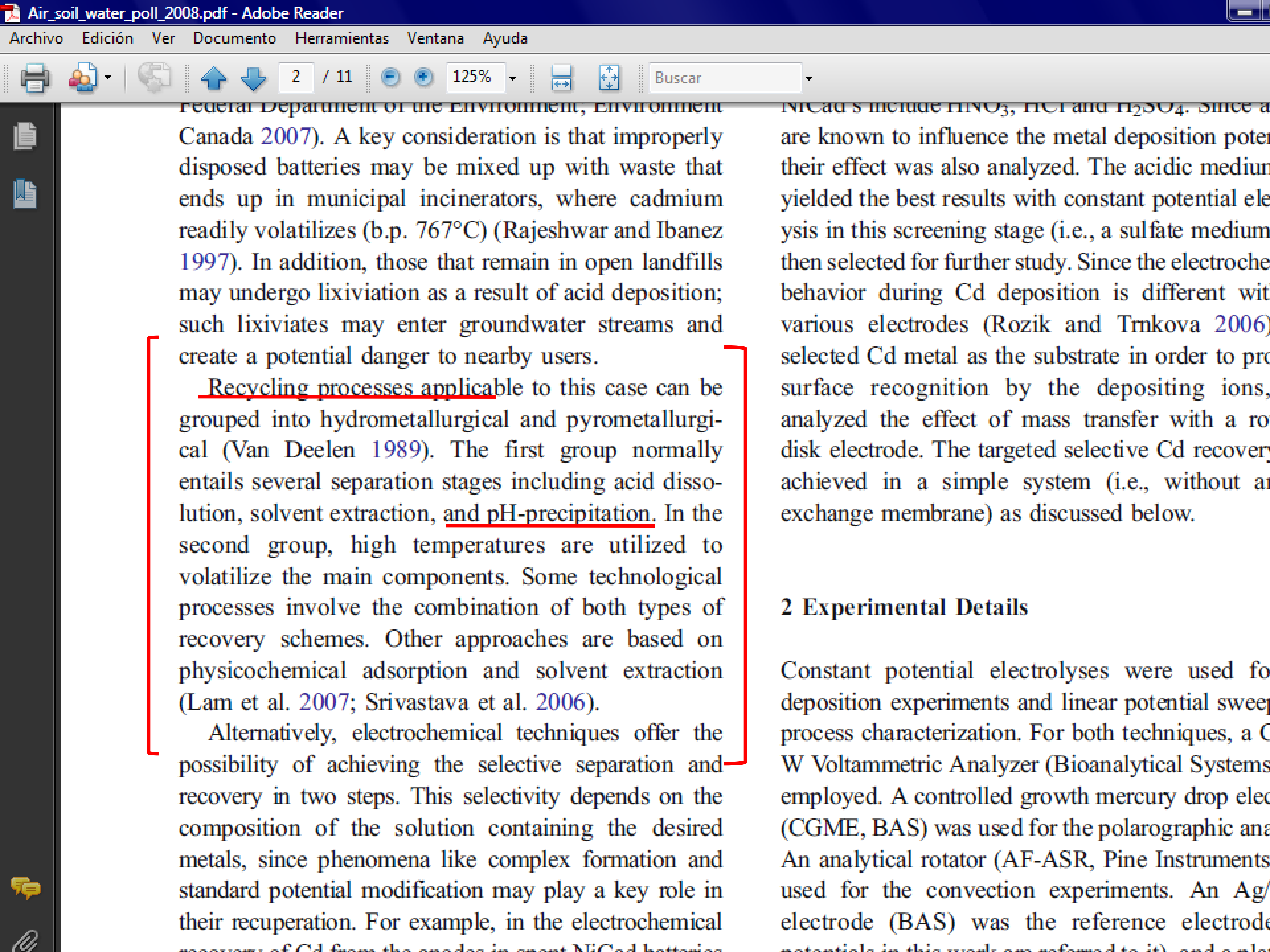
1 Introduction

Spent nickel–cadmium (NiCad) batteries still represent an important pollution problem. In fact, the US, Japan and some European countries have established tight regulations for their disposal, mainly due to the high toxicity of cadmium. Nickel compounds possess different degrees of toxicity, but that of cadmium compounds is typically more acute and bioaccumulation may represent important threats (Topperwien et al. 2007). Even though NiCad's tend to be phased out in some developed countries, they still cover a large portion of the market for emergency lights, alarms, portable electric tools, and other home and portable devices that require rechargeable batteries (Fujimoto 1997). In Canada alone, the annual shipments of NiCad consumer battery units were 9.1×10^6 in 2000, and the projection is 22.4×10^6 for 2010 (Environment Canada 2007). Such an increase is most likely due to their lower cost as compared to that of the alternative Li-ion and Ni-hydride batteries (Lam et al. 2007).

Sales of sealed NiCad batteries in the US, Japan and Europe totaled nearly 10^9 units in 1998 (Hake 1998); in spite of the lack of precise data, it can be anticipated that very few of them have been recycled. For example, only 1% of the consumer secondary



Federal Department of the Environment, Environment Canada 2007). A key consideration is that improperly disposed batteries may be mixed up with waste that ends up in municipal incinerators, where cadmium readily volatilizes (b.p. 767°C) (Rajeshwar and Ibanez 1997). In addition, those that remain in open landfills may undergo lixiviation as a result of acid deposition; such lixiviates may enter groundwater streams and create a potential danger to nearby users.

Recycling processes applicable to this case can be grouped into hydrometallurgical and pyrometallurgical (Van Deelen 1989). The first group normally entails several separation stages including acid dissolution, solvent extraction, and pH-precipitation. In the second group, high temperatures are utilized to volatilize the main components. Some technological processes involve the combination of both types of recovery schemes. Other approaches are based on physicochemical adsorption and solvent extraction (Lam et al. 2007; Srivastava et al. 2006).

Alternatively, electrochemical techniques offer the possibility of achieving the selective separation and recovery in two steps. This selectivity depends on the composition of the solution containing the desired metals, since phenomena like complex formation and standard potential modification may play a key role in their recuperation. For example, in the electrochemical

NiCad's include HNO_3, HCl and H_2SO_4. Since a
are known to influence the metal deposition poten
their effect was also analyzed. The acidic mediun
yielded the best results with constant potential ele
ysis in this screening stage (i.e., a sulfate medium
then selected for further study. Since the electroche
behavior during Cd deposition is different wit
various electrodes (Rozik and Trnkova 2006)
selected Cd metal as the substrate in order to pro
surface recognition by the depositing ions,
analyzed the effect of mass transfer with a ro
disk electrode. The targeted selective Cd recovery
achieved in a simple system (i.e., without an
exchange membrane) as discussed below.

2 Experimental Details

Constant potential electrolyses were used fo
deposition experiments and linear potential sweep
process characterization. For both techniques, a C
W Voltammetric Analyzer (Bioanalytical Systems
employed. A controlled growth mercury drop elec
(CGME, BAS) was used for the polarographic ana
An analytical rotator (AF-ASR, Pine Instruments
used for the convection experiments. An Ag/
electrode (BAS) was the reference electrode

Separación de Ni(II) y Cd(II) decimolares por precipitación ***iónica****, a pH impuesto:

Para ambos cationes:

$Ni(OH)_{2\downarrow}$ pKs = 17 ; C_{Ni} = Co = 1 mM

$Cd(OH)_{2\downarrow}$ pKs = 19; C_{Cd} = 10Co = 10 mM

* *No es necesario considerar a las especies moleculares o metalatos, i.e.,* $\alpha_{M(OH)} = 1$.

Separación de Ni(II) y Cd(II) decimolares por precipitación ***iónica**** **,** a pH impuesto:

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$Cd(OH)_{2\downarrow}$ pKs = 19; C_{Cd} = 10Co = 10 mM

Para ambos cationes:

$$Ks = [M^{2+}][OH^{-}]^{2}$$

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$Ni(OH)_{2\downarrow}$ pKs = 17 ; C_{Ni} = Co = 1 mM
$Cd(OH)_{2\downarrow}$ pKs = 19; C_{Cd} = 1Co = 10 mM

Para ambos cationes:

A partir del Kw:

$$Kw = [H^+][OH^-]$$

$$[OH^-] = Kw/[H^+]$$

Separación de Ni(II) y Cd(II) decimolares por precipitación **_iónica*_ ,** a pH impuesto:

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$$Ks = [M^{2+}][OH^{-}]^{2}$$

A partir del $Kw = [H^{+}][OH^{-}]$

$$[OH^{-}] = Kw/[H^{+}]$$

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$Cd(OH)_{2\downarrow}$ pKs = 19; C_{Cd} = 10Co = 10 mM

Para ambos cationes el Ks de los hidróxidos en función del pH:

$$Ks = [M^{2+}](Kw/[H^{+}])^{2}$$

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$Ni(OH)_{2\downarrow}$ pKs = 17 ; C_{Ni} = Co = 1 mM
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Para ambos cationes el Ks de los hidróxidos en función del pH:

$$Ks = [M^{2+}](Kw/[H^{+}])^{2}$$

Ya que $Kw = 10^{-pKw}$ y $[H^{+}] = 10^{-pH}$

Para $[M^{2+}]$ ***= S*** *(concentración metal soluble)* :

Separación de Ni(II) y Cd(II) decimolares por precipitación ***iónica**** **,** a pH impuesto:

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$Cd(OH)_{2\downarrow}$ $pK\ s = 19$; $C_{Cd} = 10Co = 10\ mM$

Para ambos cationes el Ks de los hidróxidos en función del pH:

$$Ks = \underbrace{[M^{2+}]}_{}\underbrace{(Kw/[H^{+}])^{2}}_{}$$

$$Ks = (S)\ (10^{-2pKw+2pH})$$

Separación de Ni(II) y Cd(II) decimolares por precipitación ***iónica**** **,** a pH impuesto:

$Ni(OH)_{2\downarrow}$ pKs = 17 ; C_{Ni} = Co = 1 mM
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$$Ks = (S)\ (10^{-2pKw+2pH})$$

Linearizando logarítmicamente:

Separación de Ni(II) y Cd(II) decimolares por precipitación ***iónica**** **,** a pH impuesto:

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$Cd(OH)_{2\downarrow}$ p Ks = 19; C_{Cd} = 10Co = 10 mM

Para ambos cationes el Ks de los hidróxidos en función del pH:

Linearizando logarítmicamente:

$$Ks = (S)\left(10^{-2pKw+2pH}\right)$$

$$\log S = -pKs + 2pKw - 2pH$$

Separación de Ni(II) y Cd(II) decimolares por precipitación ***iónica**** **,** a pH impuesto:

$Ni(OH)_{2\downarrow}$ pKs = 17 ; C_{Ni} = Co = 1 mM
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Para ambos cationes el Ks de los hidróxidos en función del pH:

Linearizando logarítmicamente:

$$Ks = (S)\,(10^{-2pKw+2pH})$$

$$\log S = -pKs + 2pKw - 2pH$$

$$\log S = -pKs + 28 - 2pH$$

Separación de Ni(II) y Cd(II) decimolares por precipitación ***iónica****, a pH impuesto:

$Ni(OH)_{2\downarrow}$ pKs = 17 ; C_{Ni} = Co = 1 mM
$Cd(OH)_{2\downarrow}$ pK s = 19; C_{Cd} = 10Co = 10 mM

Para el Níquel:

$$\log S = -pKs + 28 - 2pH$$

$$\log S = -17 + 28 - 2pH$$

$$\boxed{\log S = 11 - 2pH}$$

Separación de Ni(II) y Cd(II) decimolares por precipitación ***iónica**** **,** a pH impuesto:

$Ni(OH)_{2\downarrow}$ pKs = 17 ; C_{Ni} = Co = 1 mM
$Cd(OH)_{2\downarrow}$ pK s = 19; C_{Cd} = 10Co = 10 mM

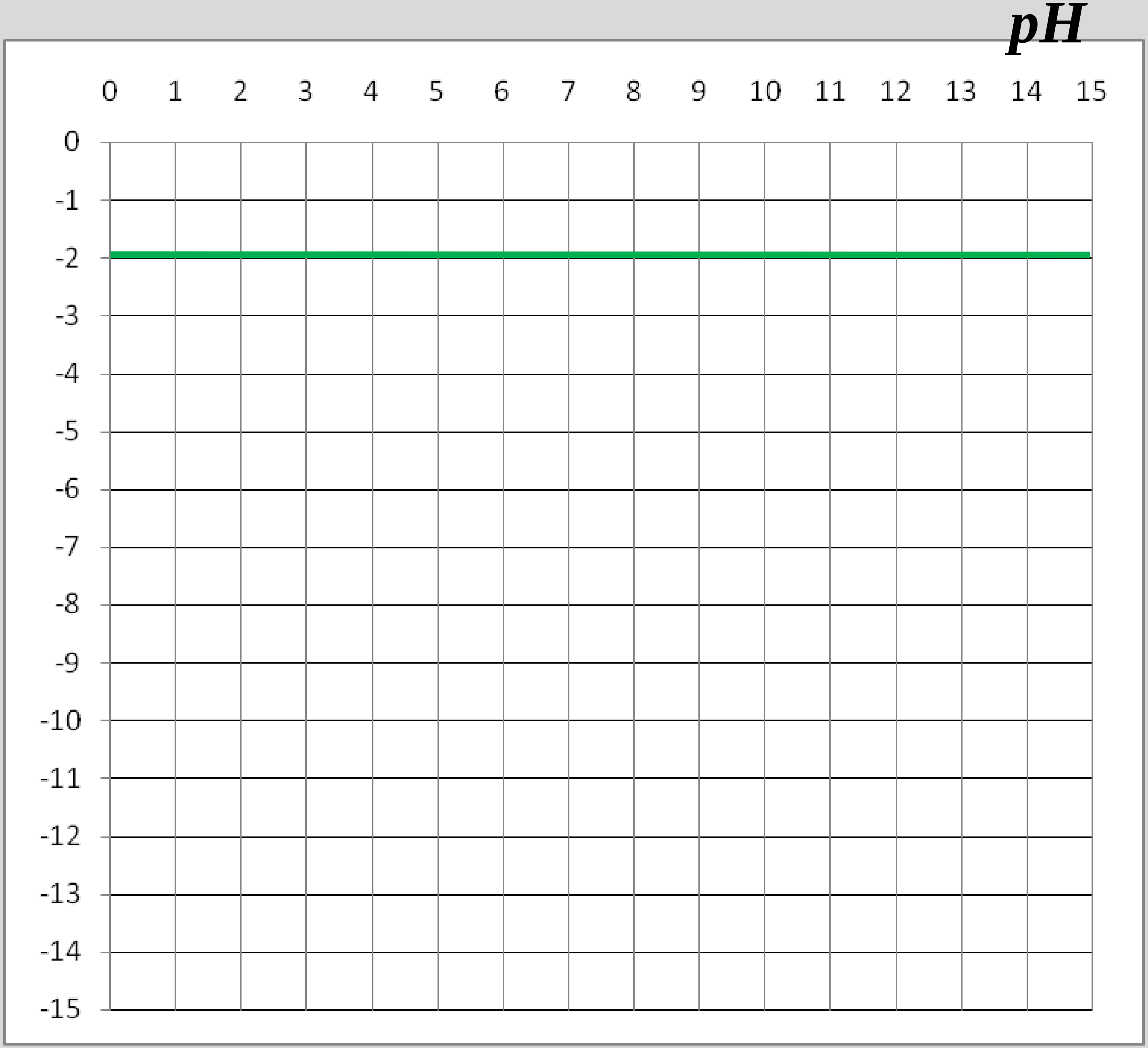
Para el Cadmio:

$$\log S = -pKs + 28 - 2pH$$

$$\log S = -19 + 28 - 2pH$$

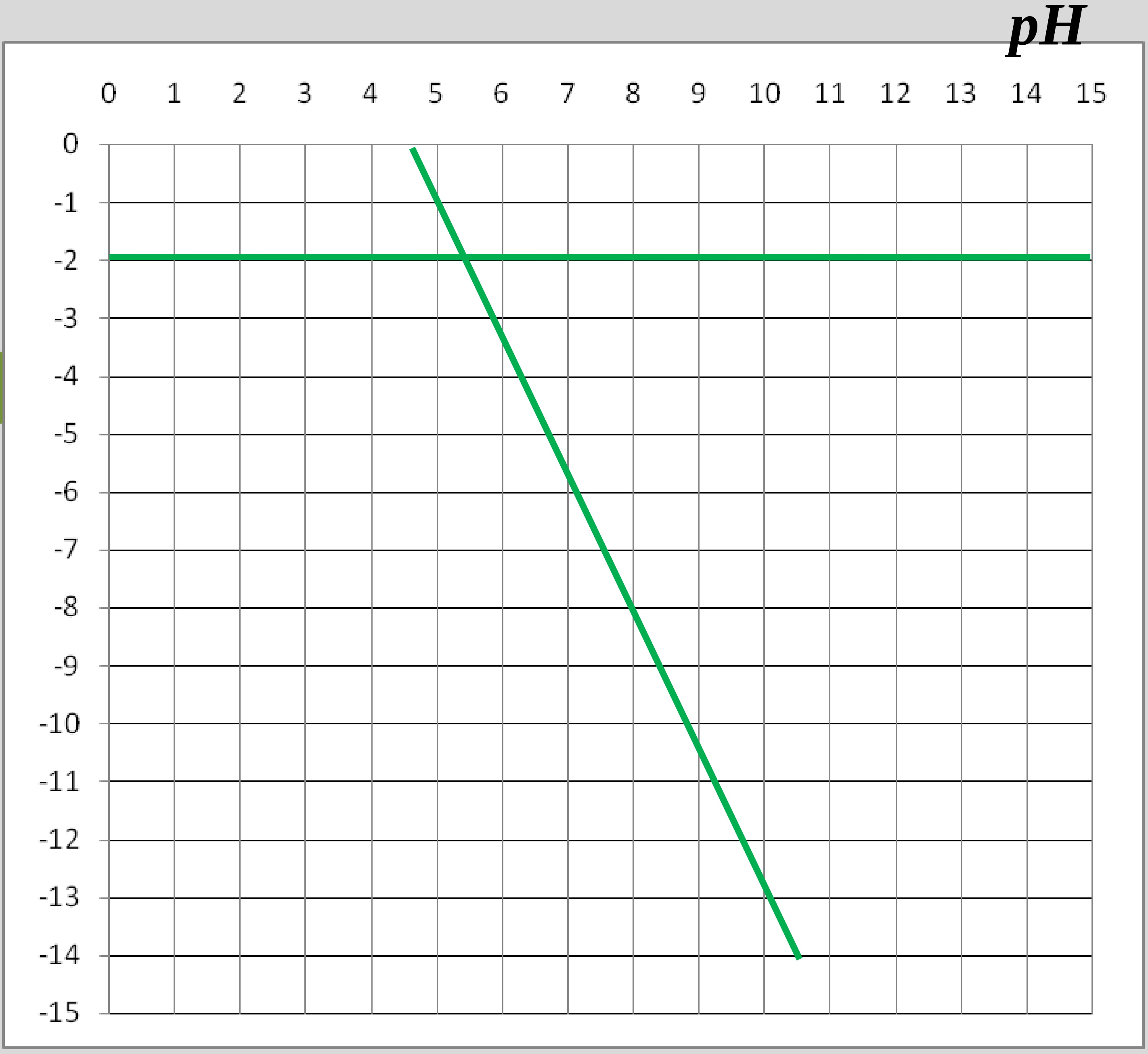
$$\boxed{\log S = 9 - 2pH}$$

Para el Cadmio:
log C_M = -2



Para el Cadmio:
log C_M = -2

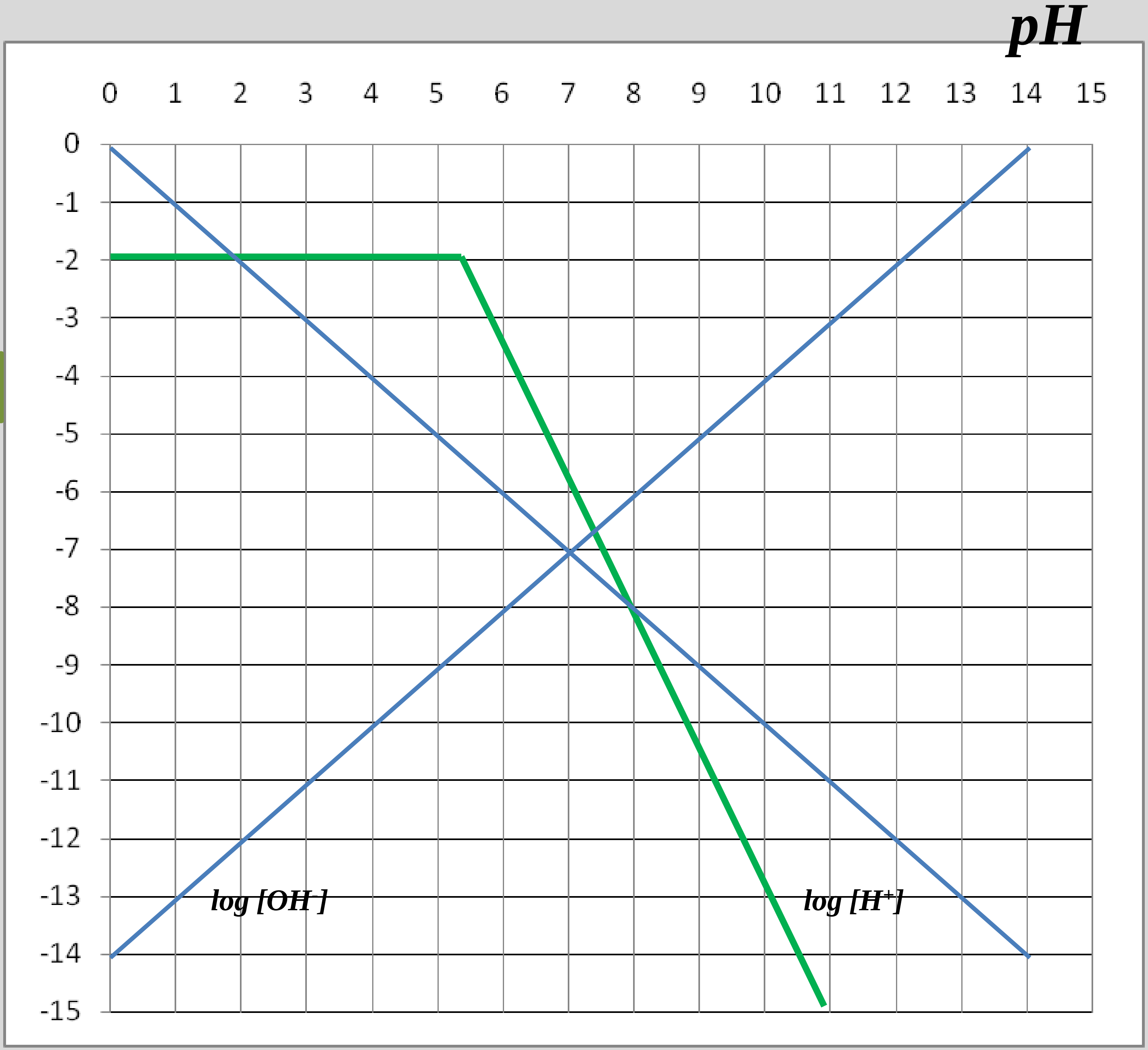
log S = 9- 2pH



log S′

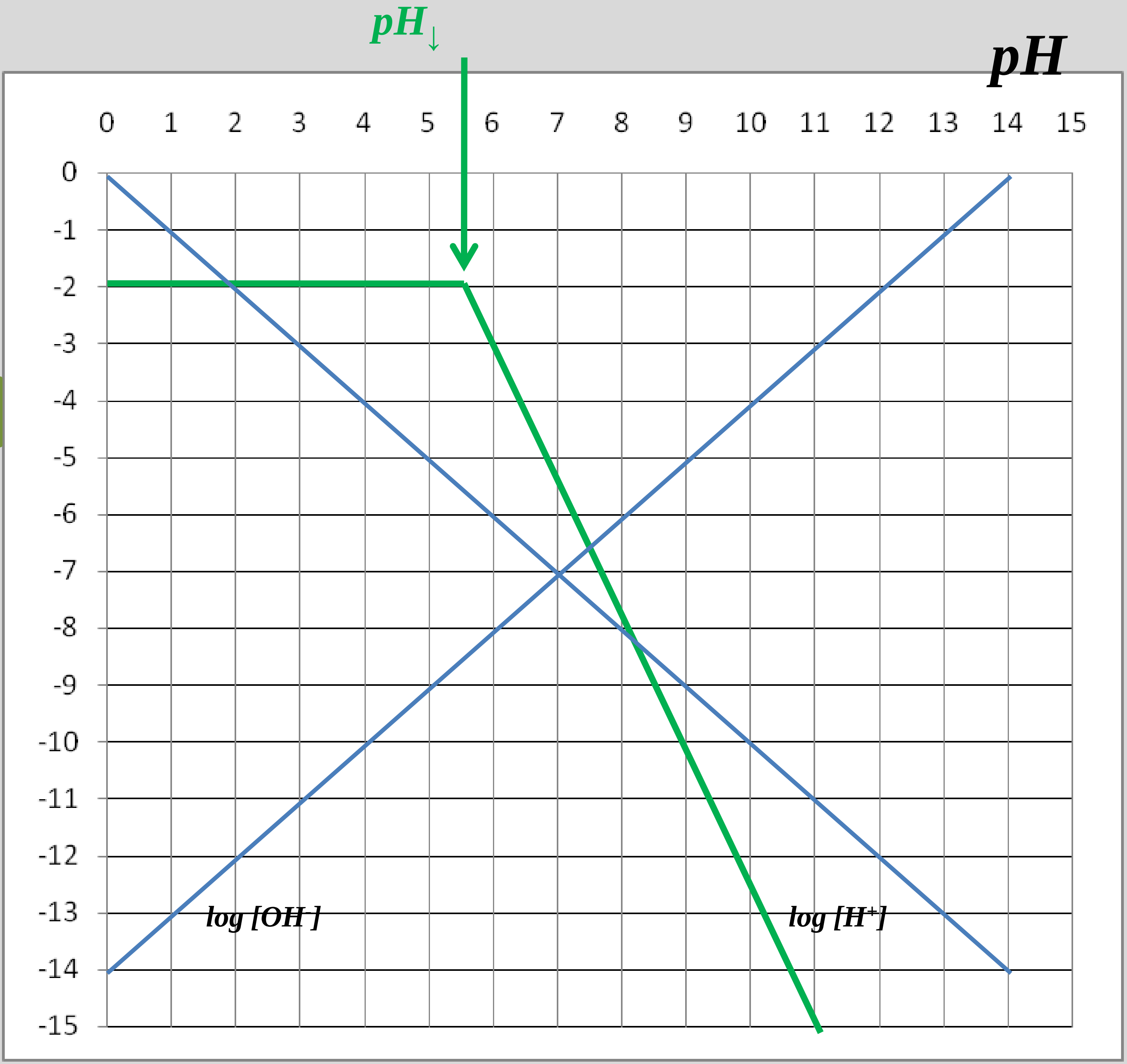
Para el Cadmio:
log C_M = -2

$$\boxed{\log S = 9 - 2pH}$$

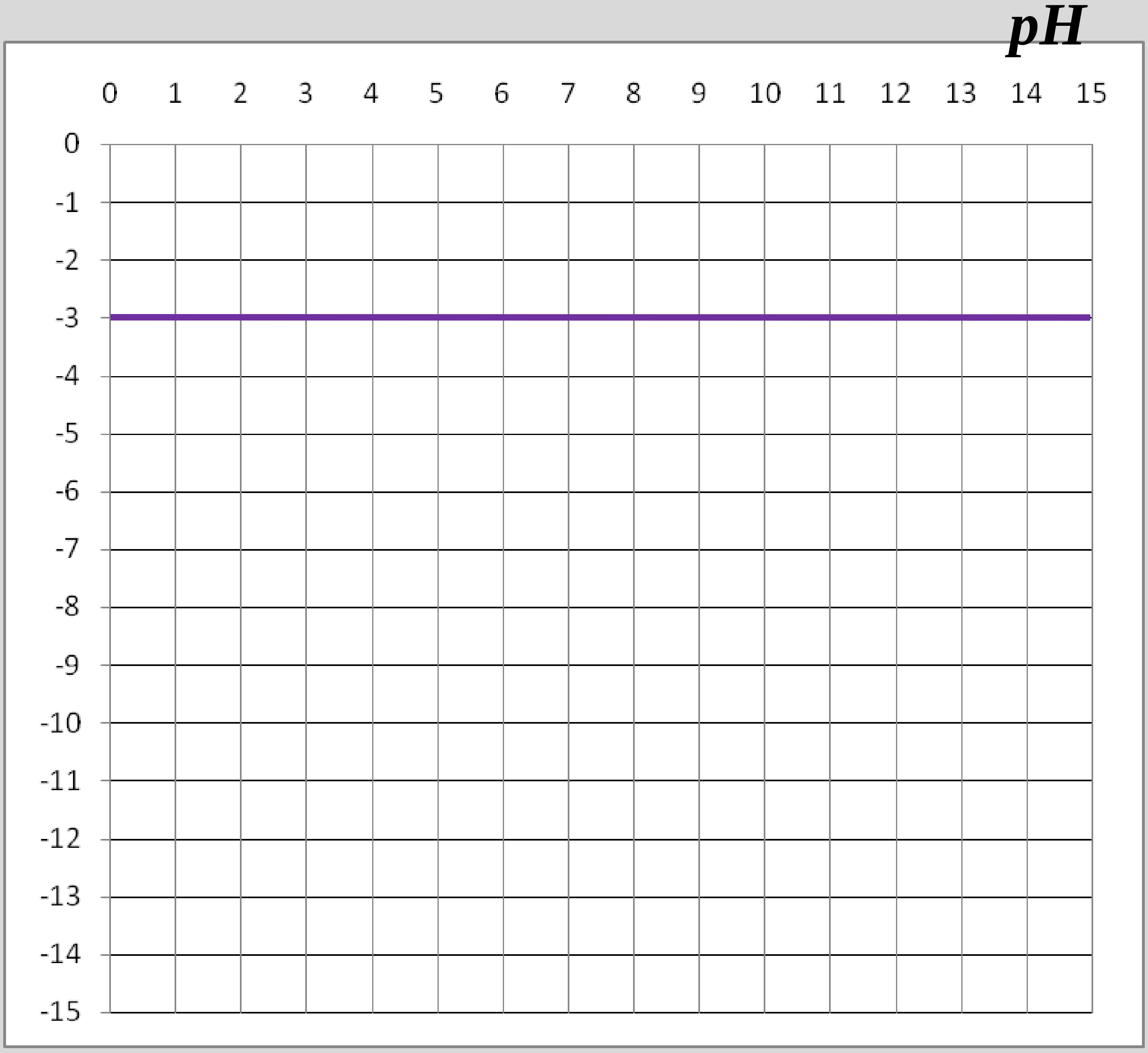


Para el Cadmio:
$\log C_M = -2$

$\log S = 9 - 2pH$



Para el Níquel:
log C_M = -3

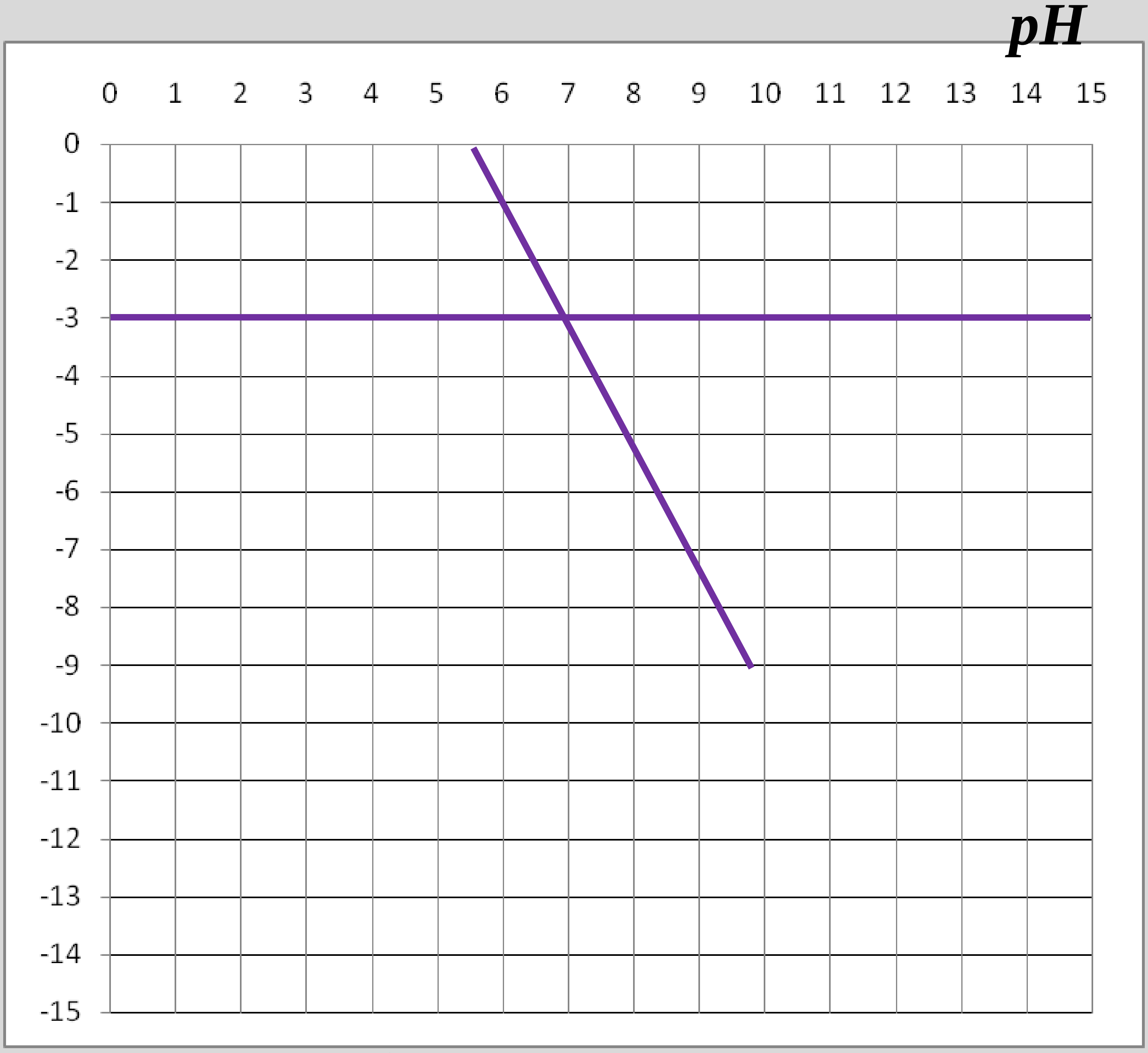


log S´

Para el Níquel:

$\log C_M = -3$

$\log S = 11 - 2pH$

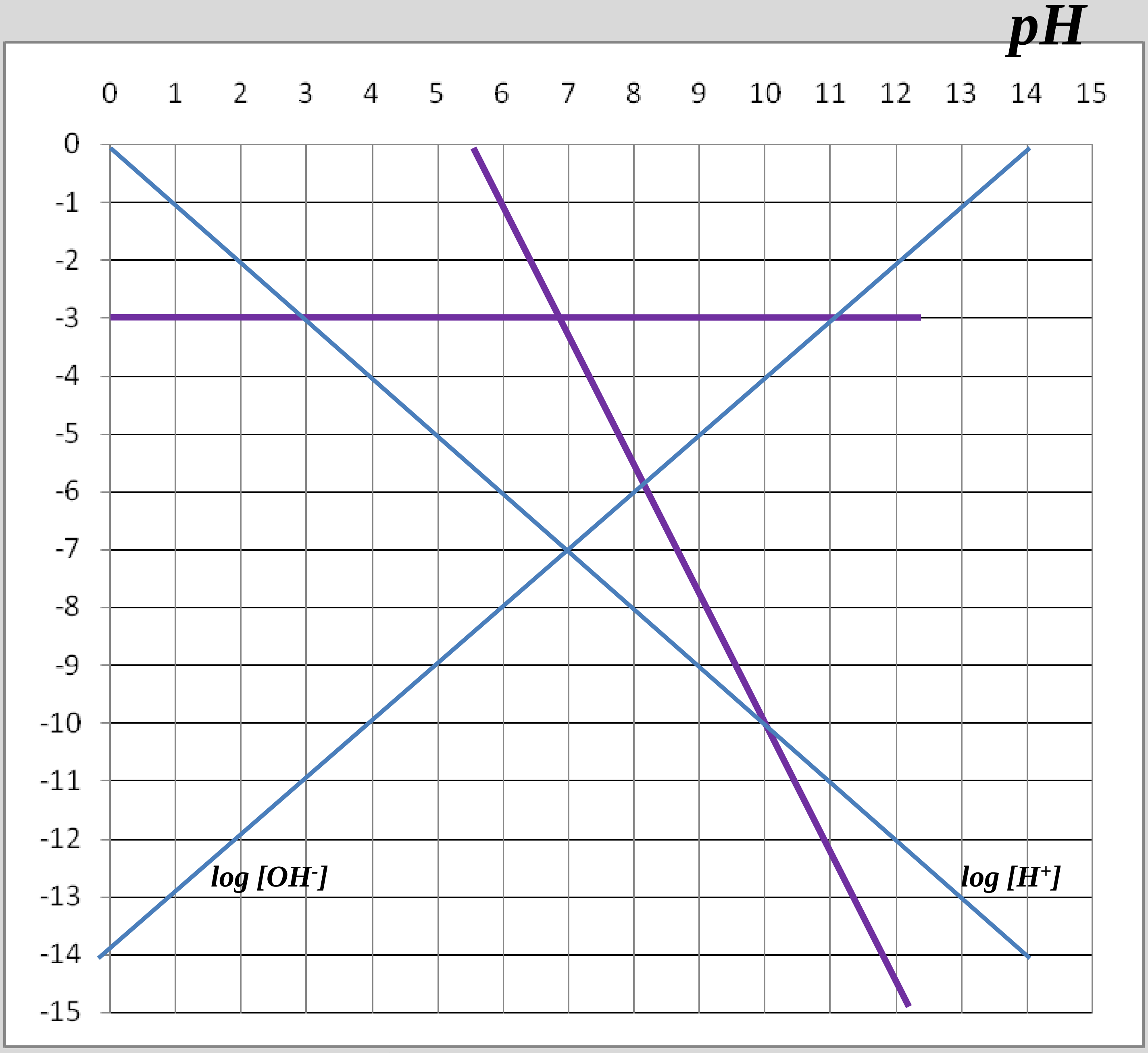


log S´

Para el Níquel:

$\log C_M = -3$

$\log S = 11 - 2pH$

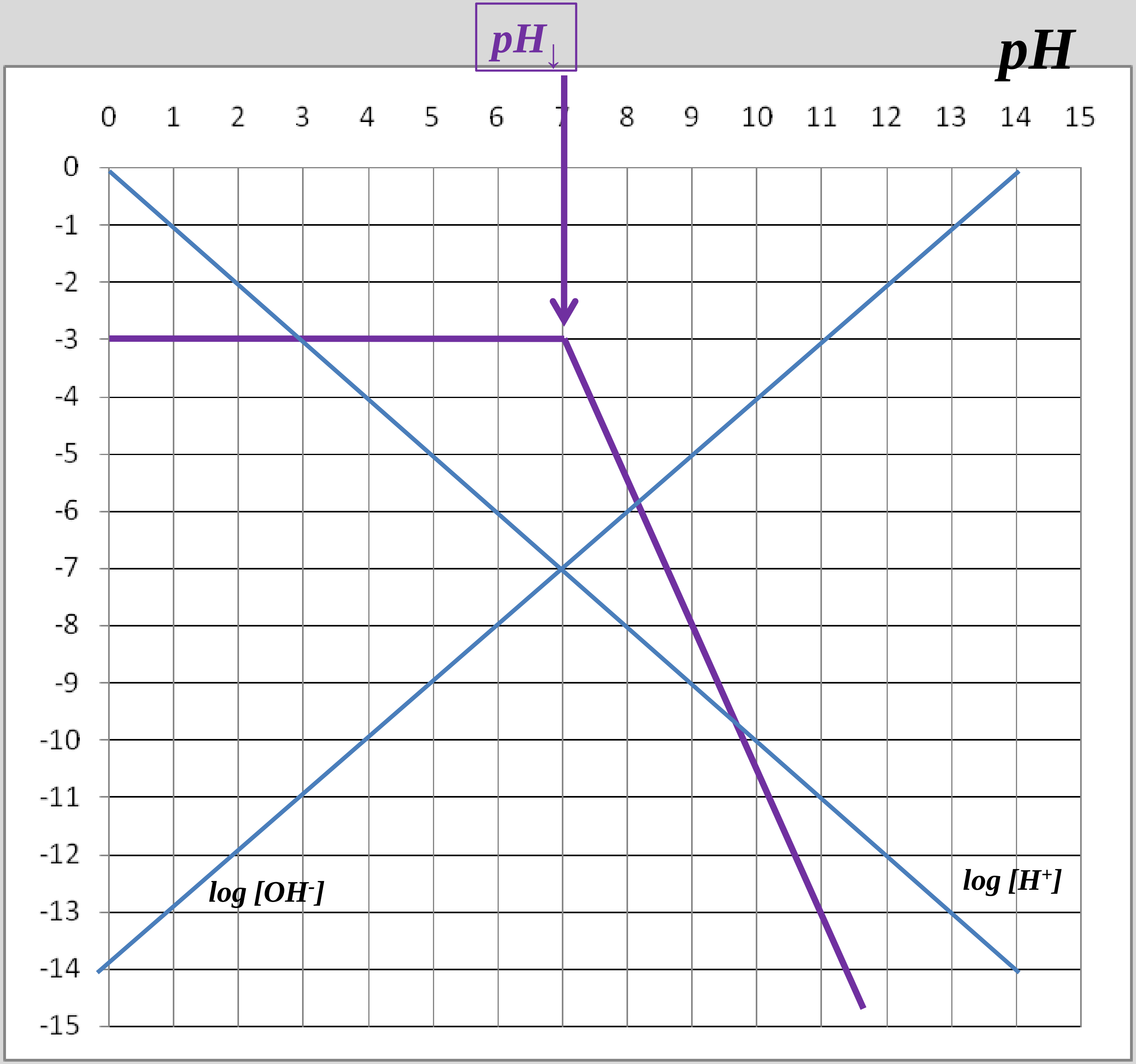


log S´

Para el Níquel:

log C_M = -3

log S = 11- 2pH



log S´

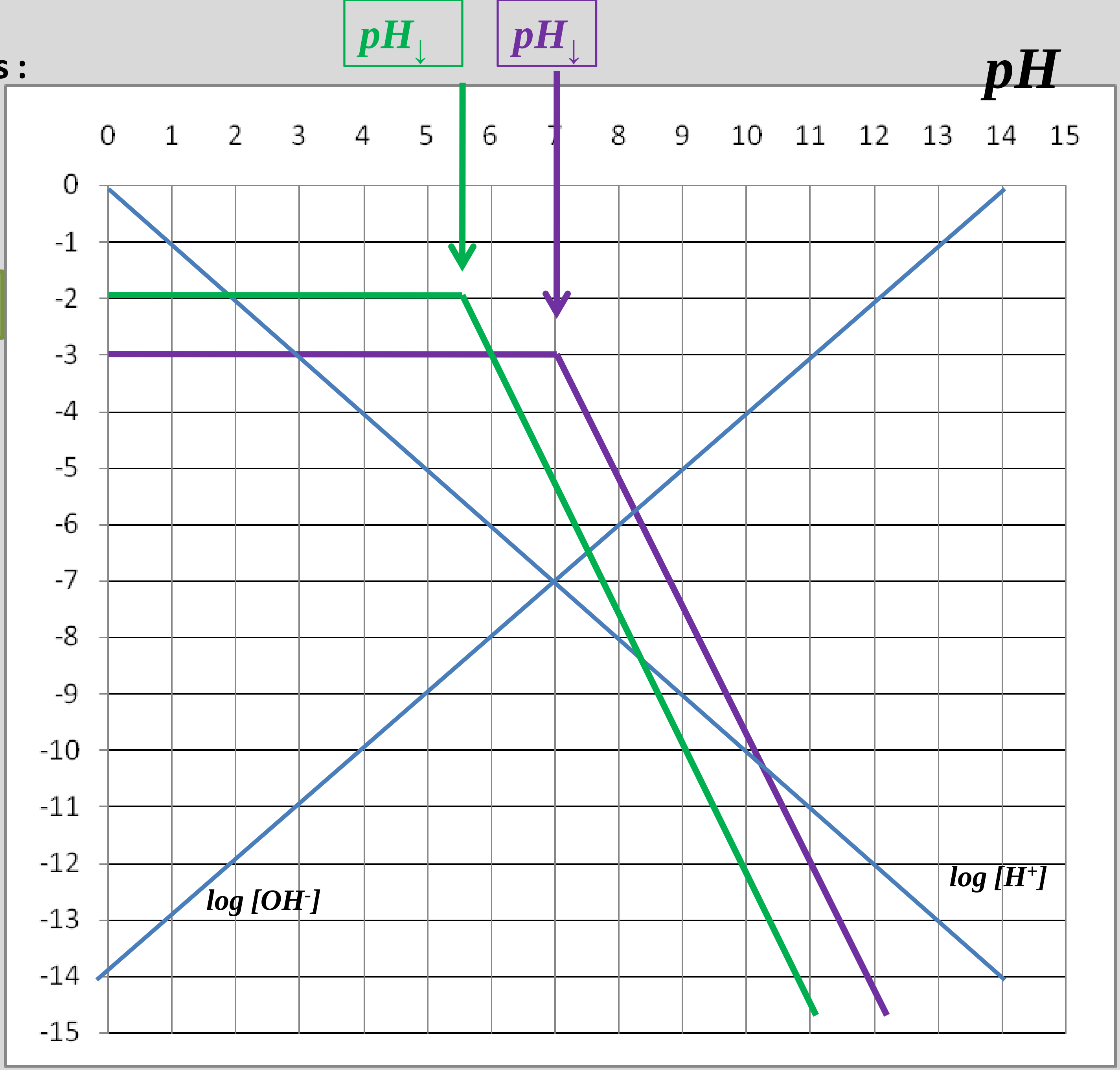
Para ambos cationes :

$\log C_{Cd} = -2$

$\log C_{Ni} = -3$

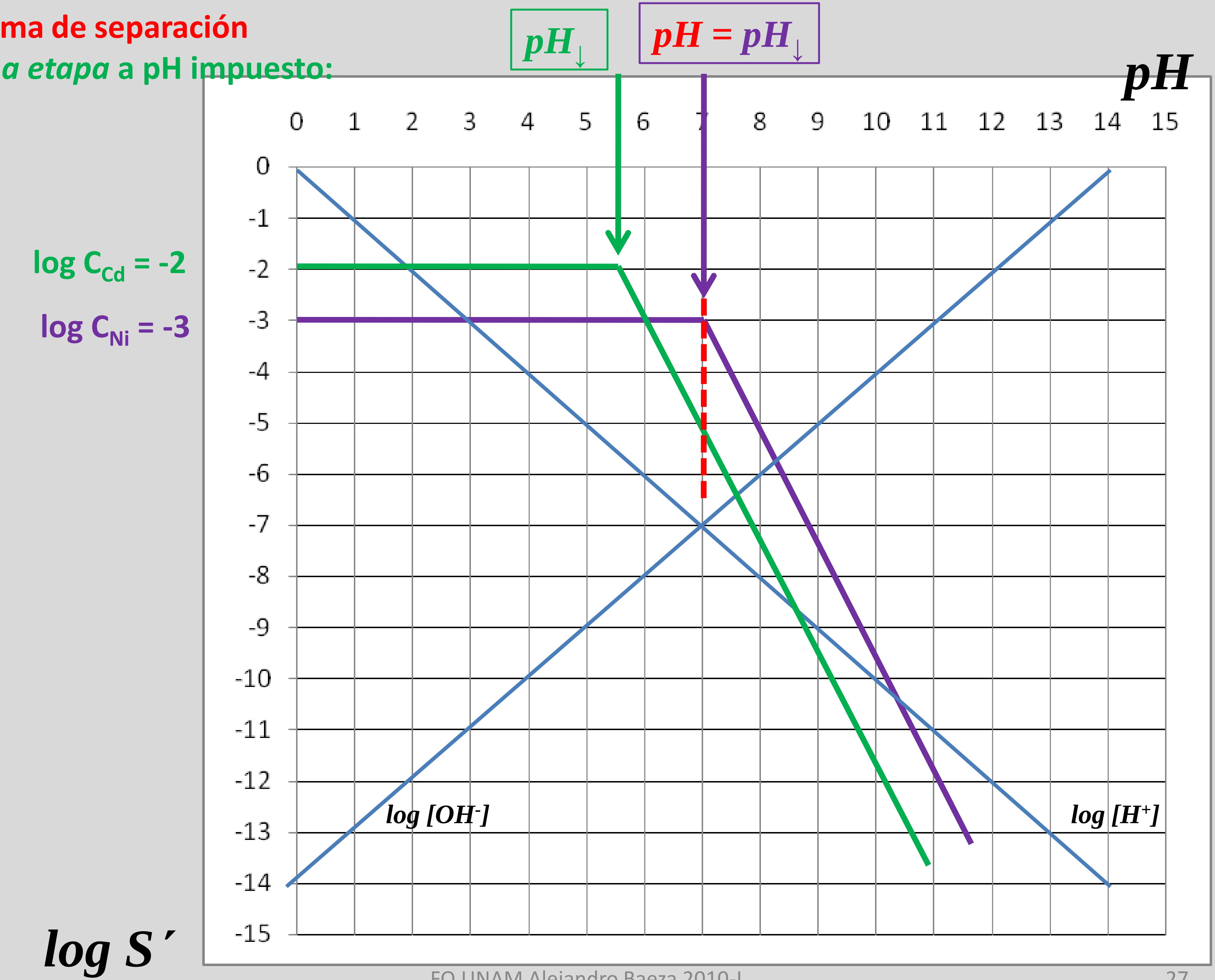
$\boxed{\log S = 9 - 2pH}$

$\boxed{\log S = 11 - 2pH}$

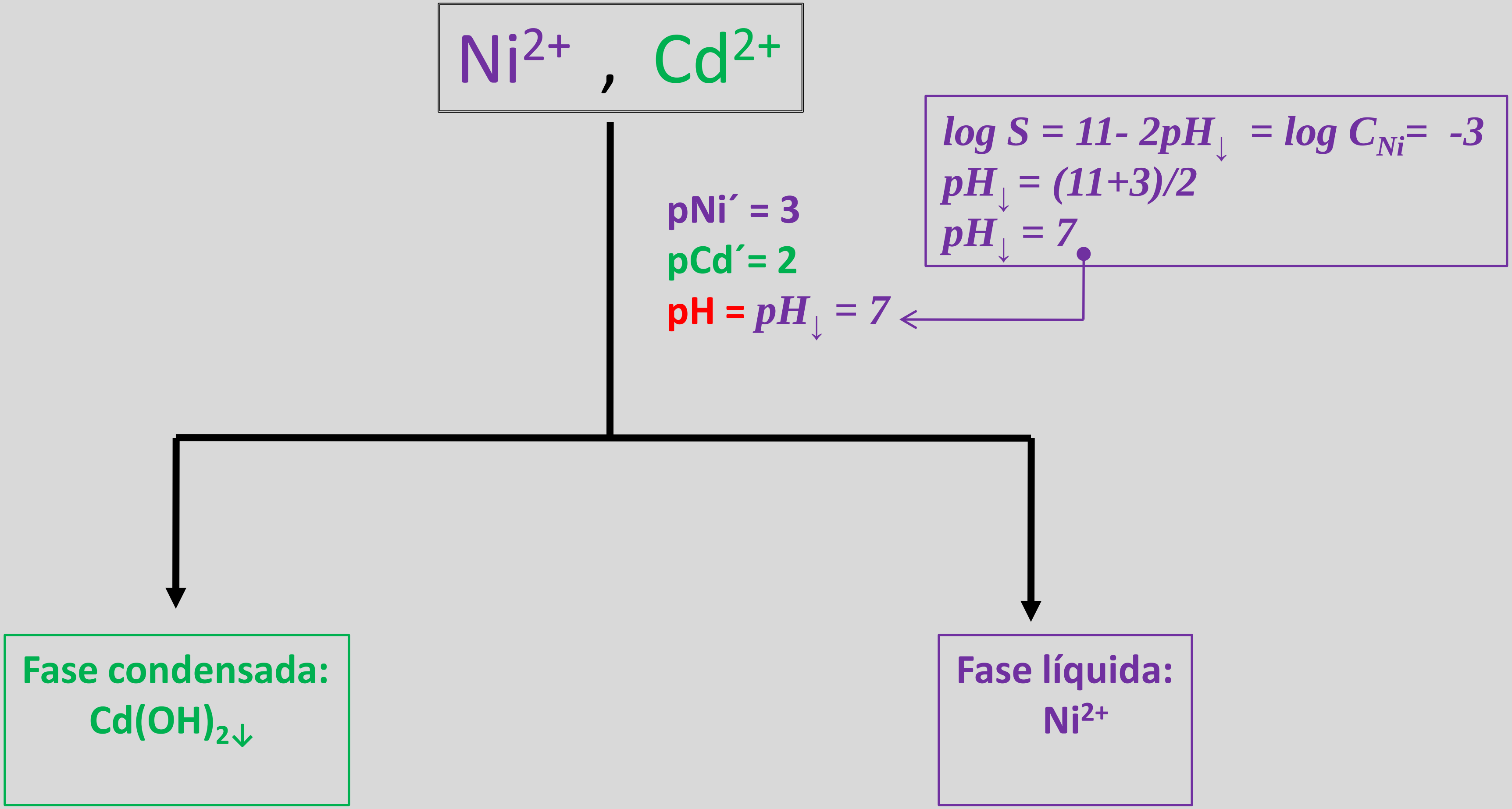


Esquema de separación

***en una etapa* a pH impuesto:**



Esquema de separación en una etapa a pH impuesto:



Ni^{2+} , Cd^{2+}

$pNi' = 3$

$pCd' = 2$

$pH = pH_{\downarrow} = 7$

$\log S = 11 - 2pH_{\downarrow} = \log C_{Ni} = -3$

$pH_{\downarrow} = (11+3)/2$

$pH_{\downarrow} = 7$

Fase condensada:
$Cd(OH)_{2\downarrow}$

Fase líquida:
Ni^{2+}

A partir de $pH = pH_{\downarrow}$ **:**

Definición de parámetro adimensional de operación analítica, *f* :

$$\boxed{f = \frac{n_{precipitada}}{n_0}}$$

A $\boldsymbol{pH = pH_{\downarrow}}$ **:**

Reacción ***operativa*** de precipitación:

$$Cd^{2+} \quad + \quad 2OH^{-} \quad \underset{}{\overset{Ks = 10^{19}}{\rightleftharpoons}} \quad Cd(OH)_{2\downarrow}$$

Inic. C_M

$$\boxed{f = \frac{n_{precipitada}}{n_0}}$$

A $pH = pH_{\downarrow}$:

Reacción ***operativa*** de precipitación,
Tabla de variación de especies:

$$Cd^{2+} \quad + \quad 2OH^{-} \rightleftarrows \quad Cd(OH)_{2\downarrow} \qquad (Ks = 10^{19})$$

Inic.	C_{Cd}		
Agreg .		fCo	
Equil.	$C_{Cd}(1-f)$		fn_0

$$[Cd^{2+}] = C_{Cd}(1-f):$$

A $pH = pH_{\downarrow}$:

Reacción ***operativa*** de precipitación,
Tabla de variación de especies:

$$Cd^{2+} + 2OH^{-} \rightleftharpoons Cd(OH)_{2\downarrow} \quad (Ks = 10^{19})$$

	Cd^{2+}	$2OH^{-}$	$Cd(OH)_{2\downarrow}$
Inic.	C_{Cd}		
Agreg .		fCo	
Equil.	$C_{Cd}(1-f)$		fn_{0}

$S = [Cd^{2+}] = C_{Cd}(1-f)$:

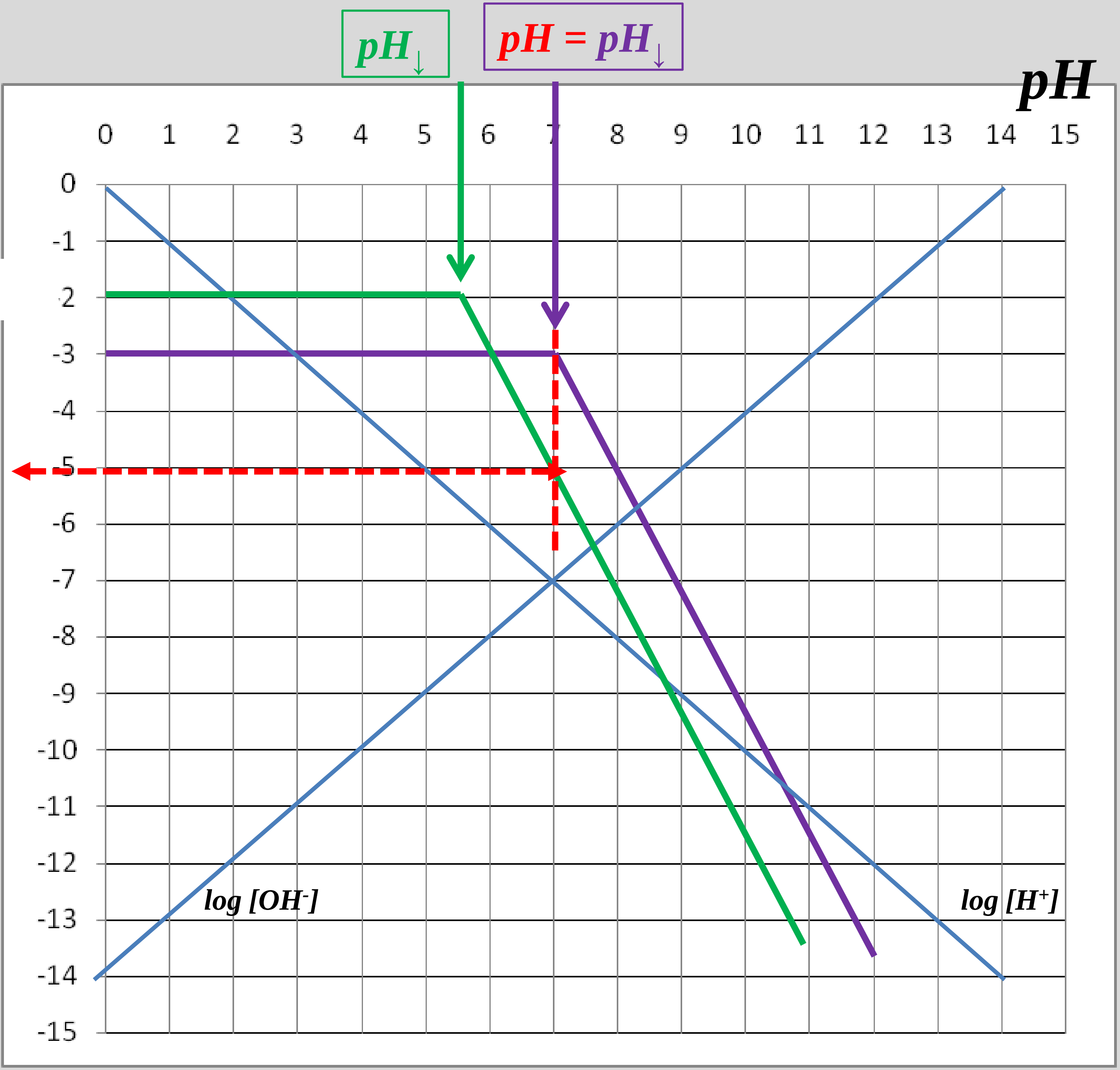
“cuando empieza a precipitar el Ni, $pH_{\downarrow}$,
queda en solución $S = [Cd^{2+}] = C_{Cd}(1-f)$:

$pH_{\downarrow}$

$pH = pH_{\downarrow}$

log C_{Cd}:

log S =log[C_{Cd}(1-*f*)]:



De la tabla de variación de especies:

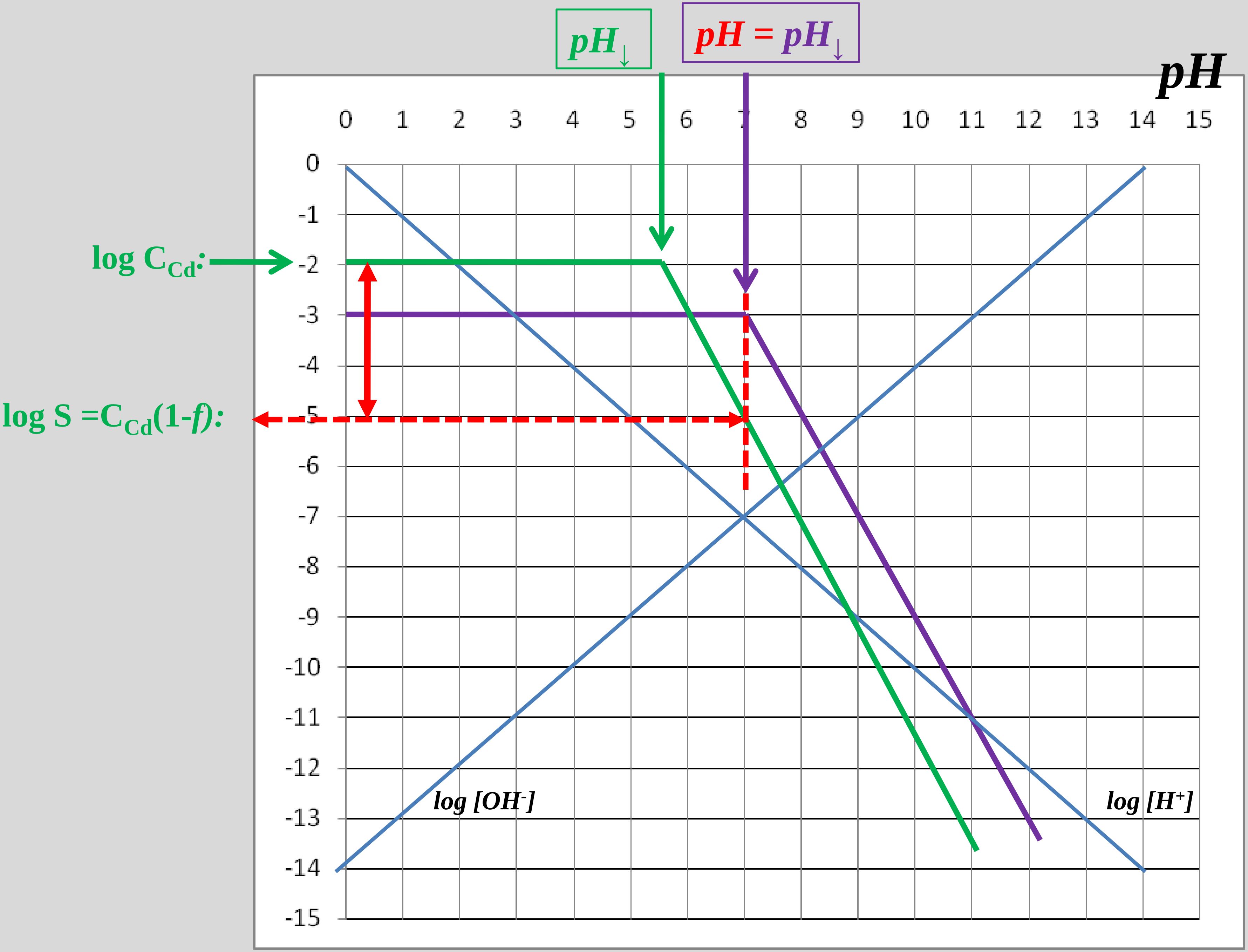
$$\log S = \log [C_{Cd}(1-f)]$$

$$\log (1-f) = \log S - \log C_{Cd}$$

$$\log S = \log [C_{Cd}(1\text{-}f)]$$

$$\log (1\text{-}f) = \log S - \log C_{Cd}$$

Gráficamente:

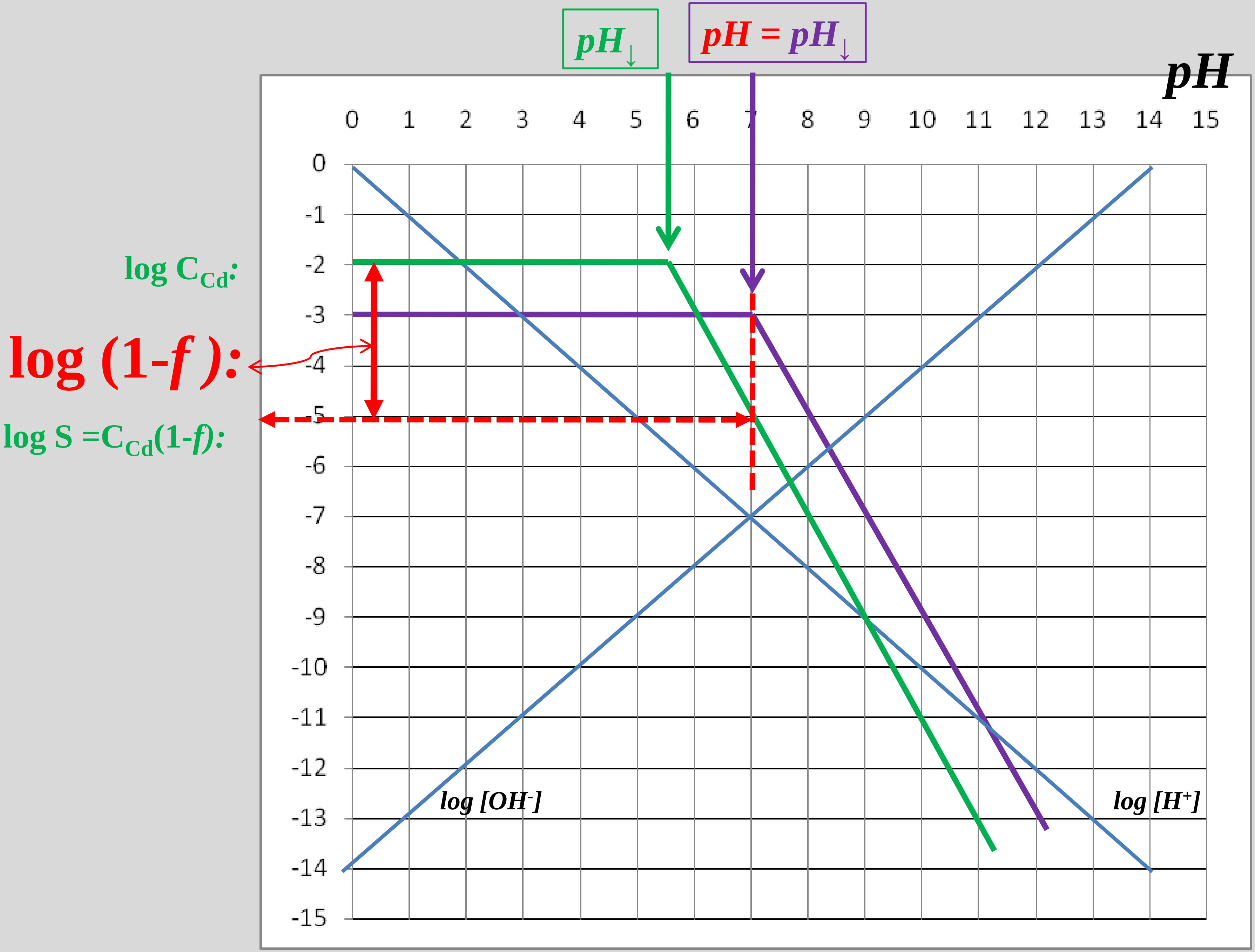


$pH_{\downarrow}$

$pH = pH_{\downarrow}$

$\log C_{Cd}$:

$\log S = C_{Cd}(1-f)$:


pH↓
pH = pH↓
pH
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
-14
-15
log C_{Cd}:
log (1-*f*):
log S =C_{Cd}(1-*f*):
log [OH^-]
log [H^+]

Gráficamente:

$$\log(1-f) \approx -3$$

$$f = 1 - 10^{-3} = 1 - 0.001$$

$$f = 0.999; \quad f\% = 99.90\%$$

Algebraicamente:

Para el níquel:

$$Ks = [Ni^{2+}][OH^{-}]^{2} = 10^{-17};$$

$$A \ \ pH_{\downarrow} = 7.0, \quad pOH_{\downarrow} = 7.0$$

$$C_{Ni}\,[OH^{-}]^{2} = 10^{-17}$$

$$(10^{-3})(10^{-7})^{2} = 10^{-17} = Ks.$$

Algebraicamente:

Para el cadmio:

$\mathbf{Ks = [Cd^{2+}][OH^{-}]^2 = 10^{-19};}$

A $pH_{\downarrow} = 7.0$, $pOH_{\downarrow} = 7.0$

$\mathbf{\mathit{S}\,[OH^{-}]^2 = 10^{-19}}$

$\mathbf{(S)(10^{-7})^2 = 10^{-19}}$

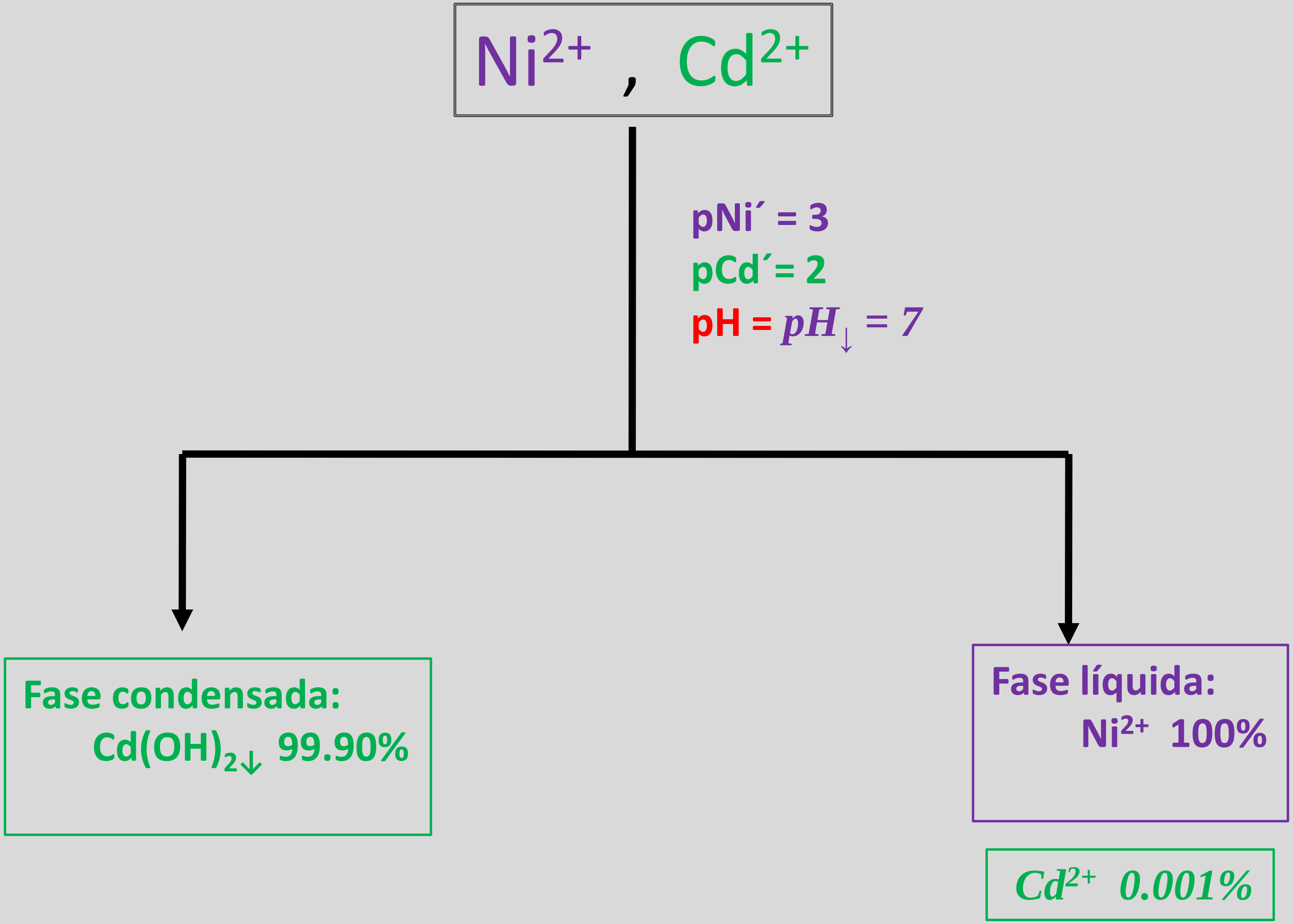
$\mathbf{S = 10^{-5}\ mol/L}$

$\mathbf{1\text{-}\mathit{f} = (S/C_{Cd}) = (10^{-5}/10^{-2}) = 10^{-3}}$

$f = 1 - 0.001 = 0.999$

$f\,\% = 99.90\%$

Esquema de separación en una etapa a pH impuesto:



Ni^{2+} , Cd^{2+}

$pNi' = 3$

$pCd' = 2$

$pH = pH_{\downarrow} = 7$

Fase condensada:
$Cd(OH)_{2\downarrow}$ 99.90%

Fase líquida:
Ni^{2+} 100%

Cd^{2+} 0.001%

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