

Progress of Yara`s tasks

Hydromet project meeting

June 15, 2016



UiO : **University of Oslo**

Alessio Vascon,

Anne-Marie Skramstad, Dag Øistein Eriksen, Grethe Wibetoe, Jon Petter Omtvedt

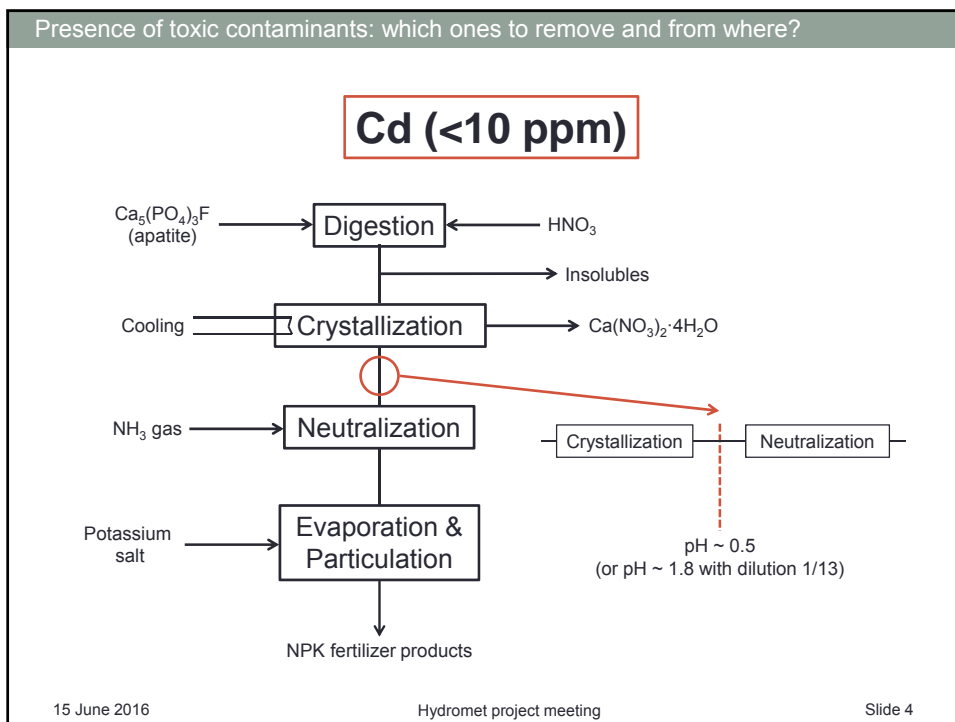
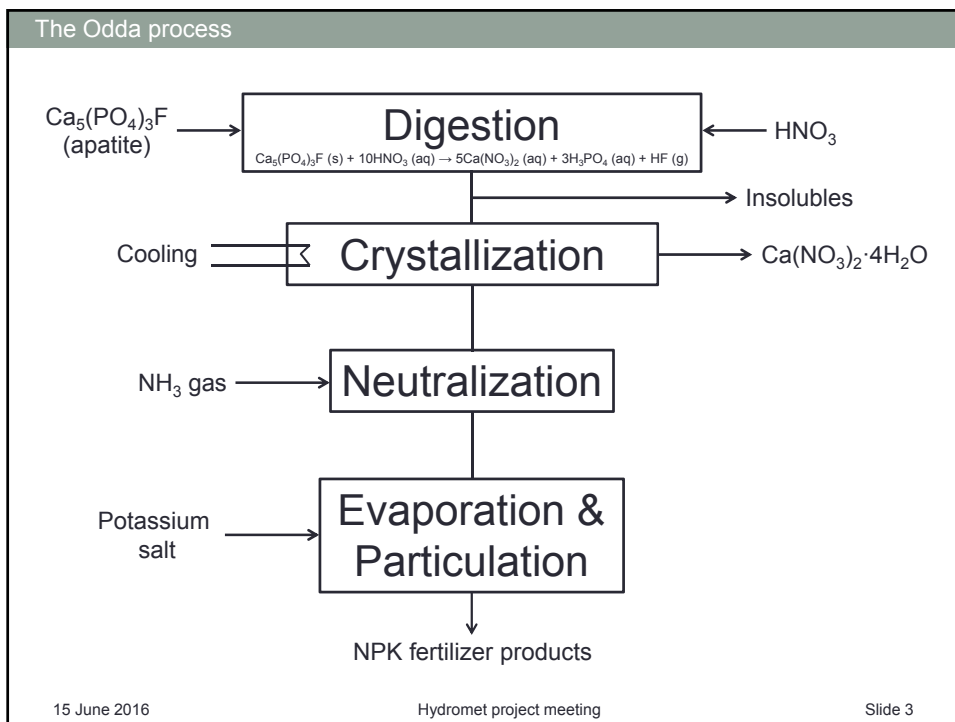


Institute for Energy Technology

Alexander Krivokapic, Liv Stavsetra

Outline

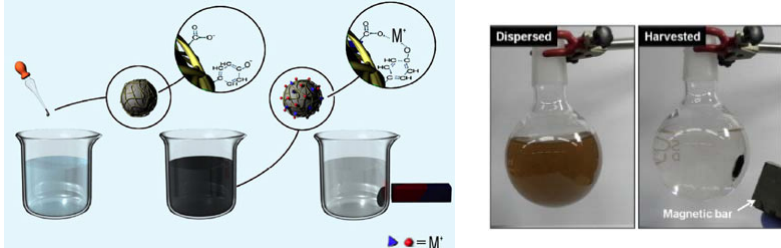
- The Odda process: challenges and possible solutions
- Bibliographic research: new results
- KELEX 100: chemical stability studies
- KELEX 100: solvent extraction studies
- Magnetic particles: stability tests in Yara`s mother liquors
- ICP-OES analysis of Yara`s industrial mother liquor
- Summary



How to remove Cd?

Magnetic particles

(particles with a magnetic core coated with a surface coating and functional groups chosen for the specific application)



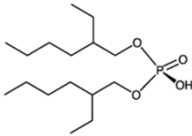
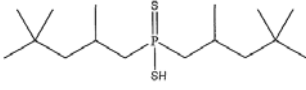
**Functional groups
for Cd removal?**

➔

**Solvent extraction
studies**

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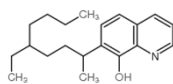
Previous solvent extraction studies (Håvard Kristiansen)

	+ kerosene ➔	$\text{HNO}_3/\text{H}_3\text{PO}_4$ synthetic solutions (pH 0.5-2) OK	Yara's mother liquor (pH ~2) no extraction (poor selectivity)
	+ kerosene ➔	OK (but undergoes oxidation)	—
HDEHP di-(2-ethylhexyl)phosphoric acid			
Cyanex 301 di-(2,4,4-trimethyl pentyl)phosphinic acid			

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New bibliographic results: KELEX 100

Organic phase

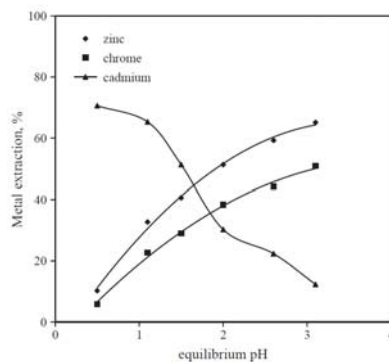


KELEX 100
7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline

+ kerosene
with (10% vol)
n-decanol

Aqueous phase

H_3PO_4 sol.
(pH 0.5-4)



A. Mellah et al., Hydrometallurgy 81 (2006) 100-103

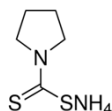
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New bibliographic results: ammonium pyrrolidine dithiocarbamate

Organic phase

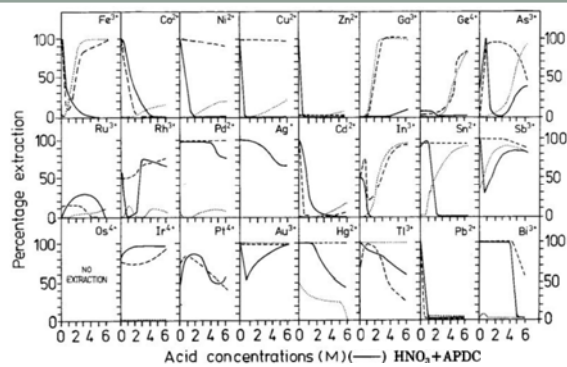


Ammonium pyrrolidine dithiocarbamate
(APDC)

+ Methyl
isobutyl ketone
(MIBK)

Aqueous phase

HNO_3 sol.
(0-6 M)



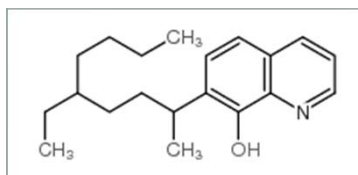
R. Brooks et al., Analytica Chimica Acta 217 (1989) 165-170

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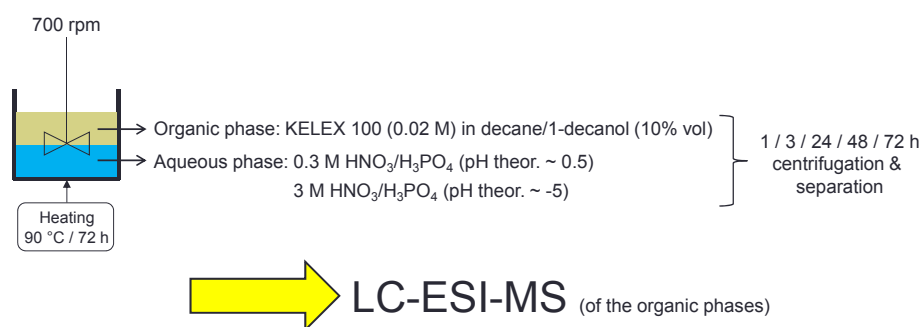
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KELEX 100: chemical stability studies



KELEX 100
7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline



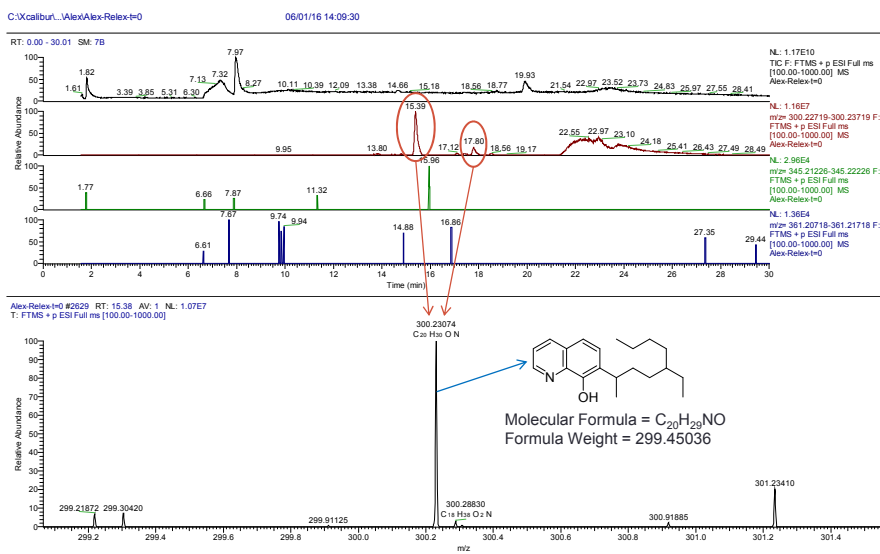
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KELEX 100 chemical stability studies: LC-ESI-MS results

Reference organic phase: KELEX 100 (0.02 M) in decane/1-decanol (10% vol)

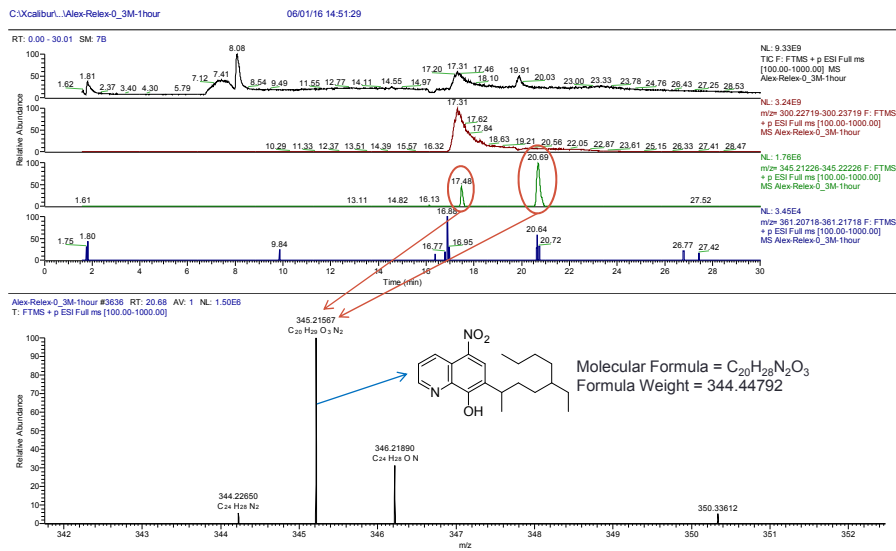


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KELEX 100 chemical stability studies: LC-ESI-MS results

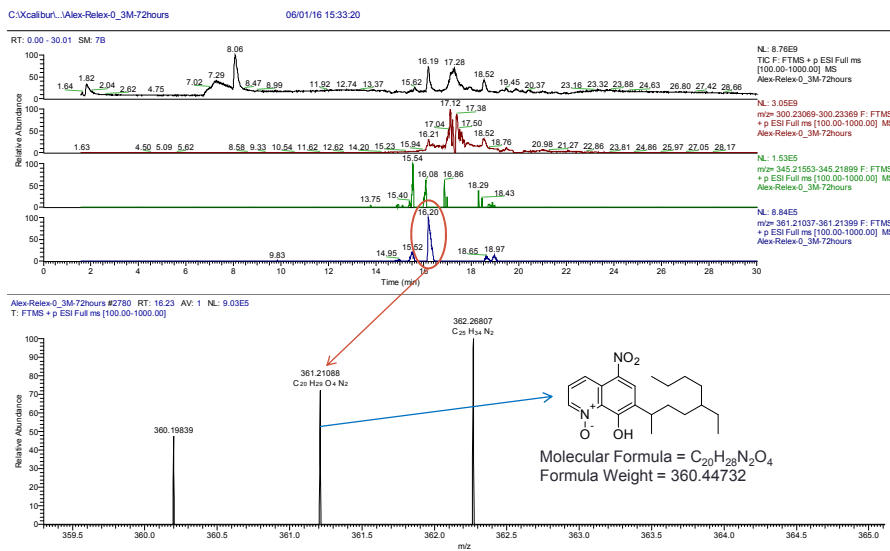
Organic phase after reaction with 0.3 M HNO₃/H₃PO₄ solution for 1h at 90 °C

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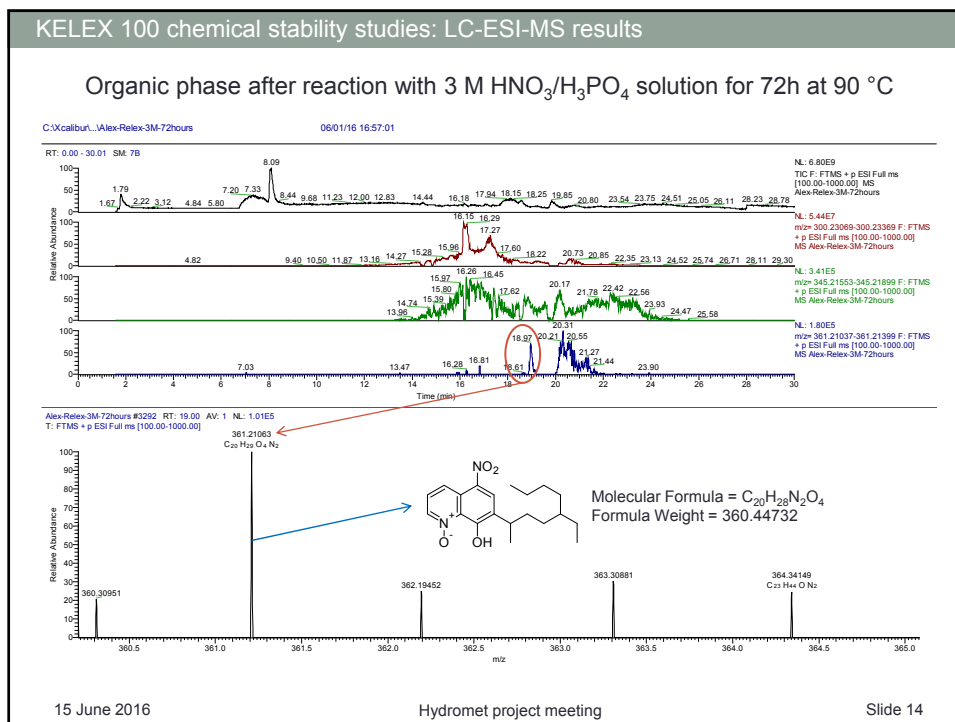
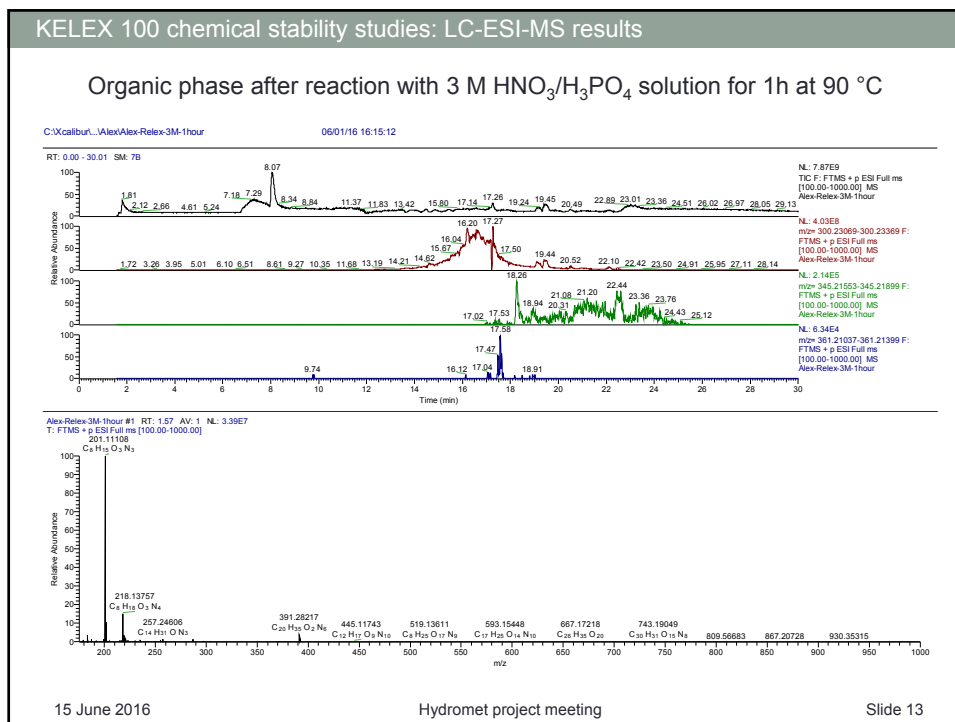
KELEX 100 chemical stability studies: LC-ESI-MS results

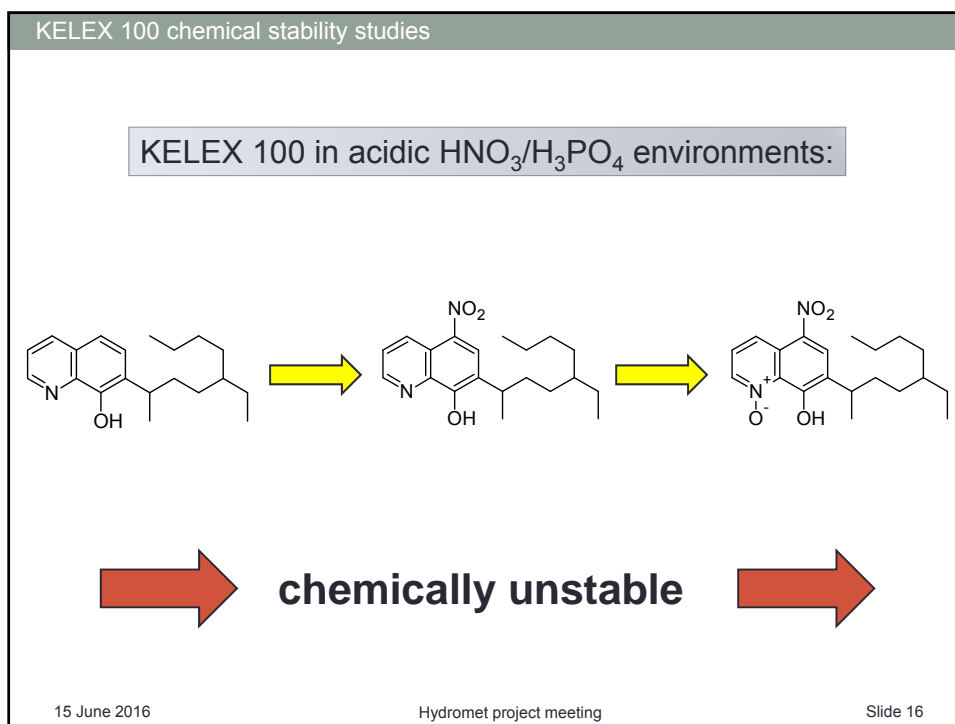
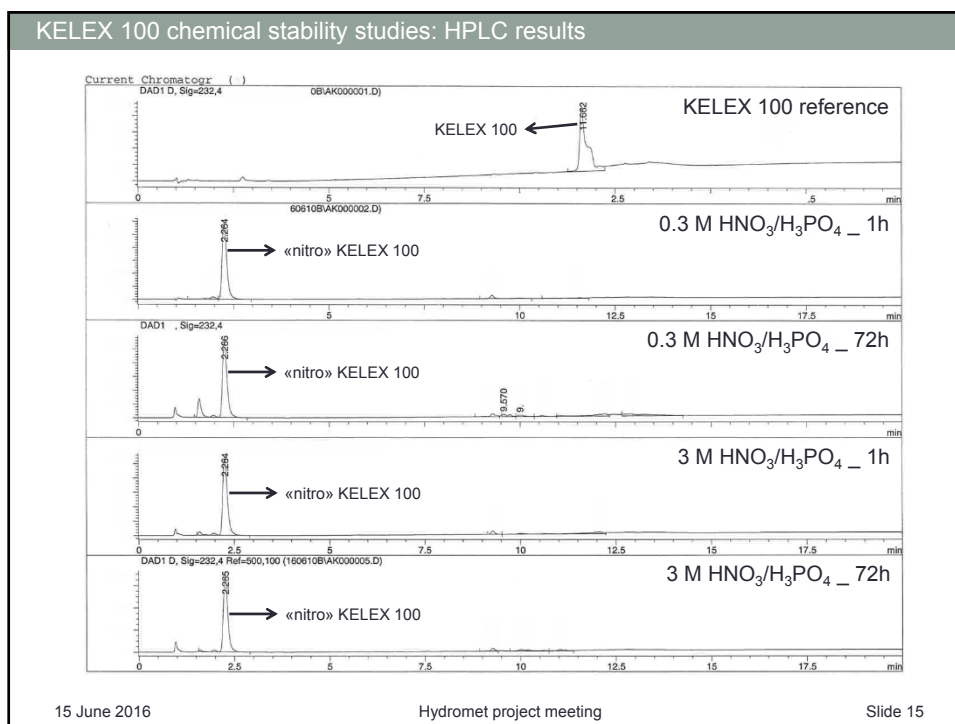
Organic phase after reaction with 0.3 M HNO₃/H₃PO₄ solution for 72h at 90 °C

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KELEX 100: solvent extraction studies




KELEX 100 (0.02 M)
in decane/1-decanol (10% vol)

+




$\text{HNO}_3/\text{H}_3\text{PO}_4$ or H_3PO_4 solutions
(containing 10 ppm Cd)
at different pH values


=



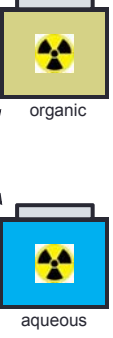
^{109}Cd in
0.05 M HNO_3
O/A: 1/1




shaking
(according to proper
equilibrium kinetics study)



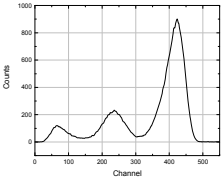
centrifugation



organic
aqueous



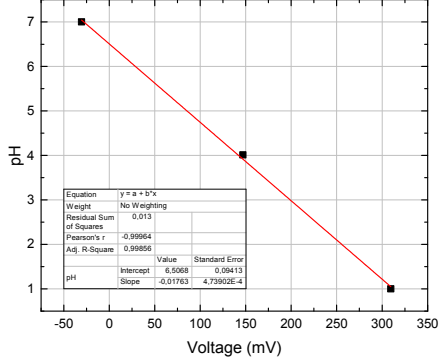
liquid scintillation counting
(after proper efficiency calibration)



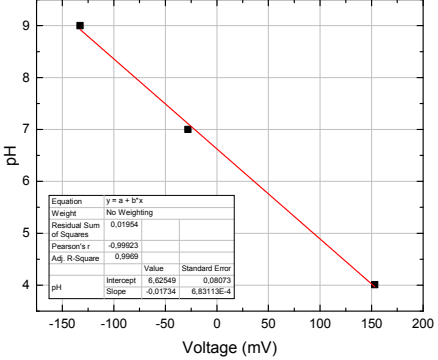
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KELEX 100: solvent extraction studies

pH measurement



Equation		
Equation	$y = a + b \cdot x$	
Weight	No Weighting	
Residual Sum of Squares	0.013	
Pearson's r	-0.99964	
Adj. R-Square	0.99986	
	Value	Standard Error
pH	Intercept	6.5068
	Slope	-0.01763
		4.73902E-4

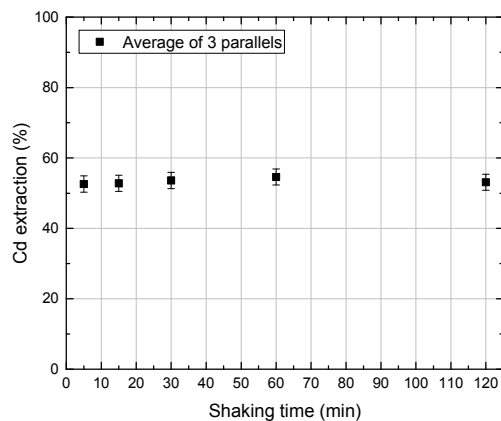


Equation		
Equation	$y = a + b \cdot x$	
Weight	No Weighting	
Residual Sum of Squares	0.01954	
Pearson's r	-0.99923	
Adj. R-Square	0.9999	
	Value	Standard Error
pH	Intercept	6.62549
	Slope	-0.01754
		6.83119E-4

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KELEX 100: solvent extraction studies from mixed $\text{HNO}_3/\text{H}_3\text{PO}_4$ solutions

Equilibrium kinetics study



O: KELEX 100 (0.02 M)
in decane/1-decanol (10% vol)

A: $\text{HNO}_3/\text{H}_3\text{PO}_4$ sol.
eq. pH 7.1 ± 0.1

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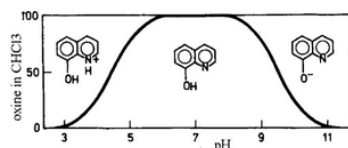
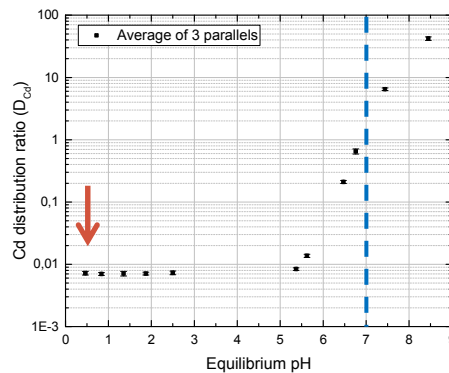
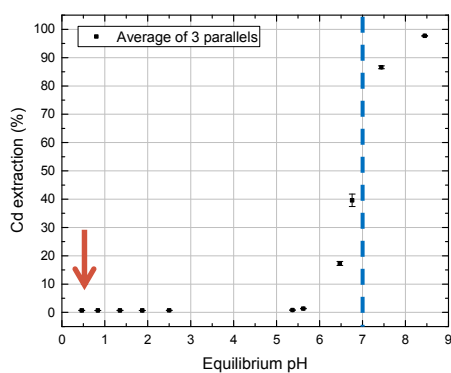
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KELEX 100: solvent extraction studies from mixed $\text{HNO}_3/\text{H}_3\text{PO}_4$ solutions

O: KELEX 100 (0.02 M)
in decane/1-decanol (10% vol)

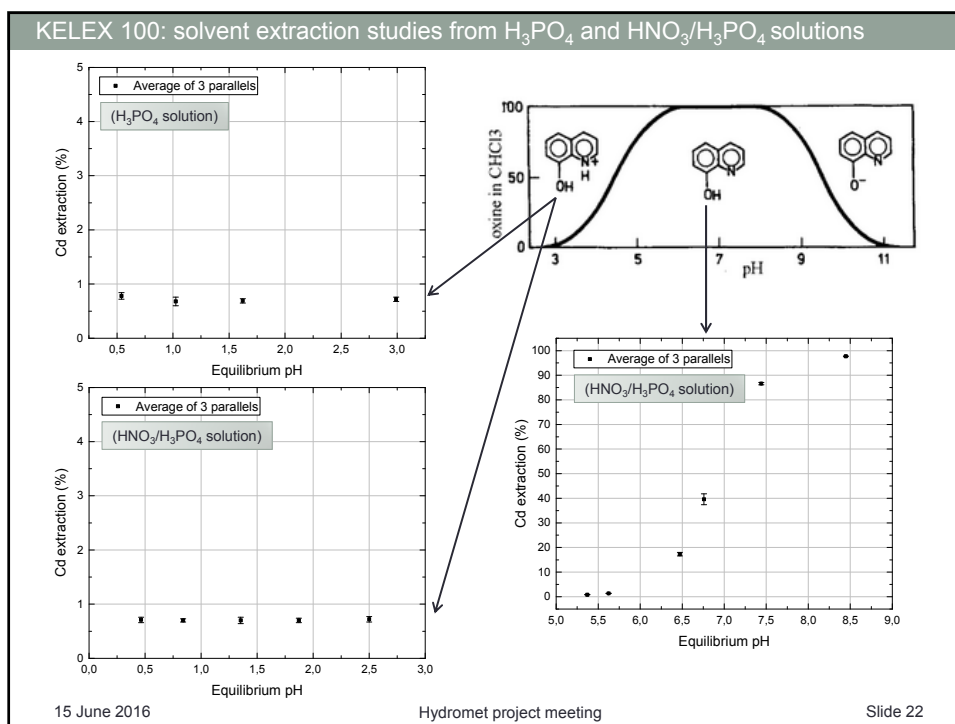
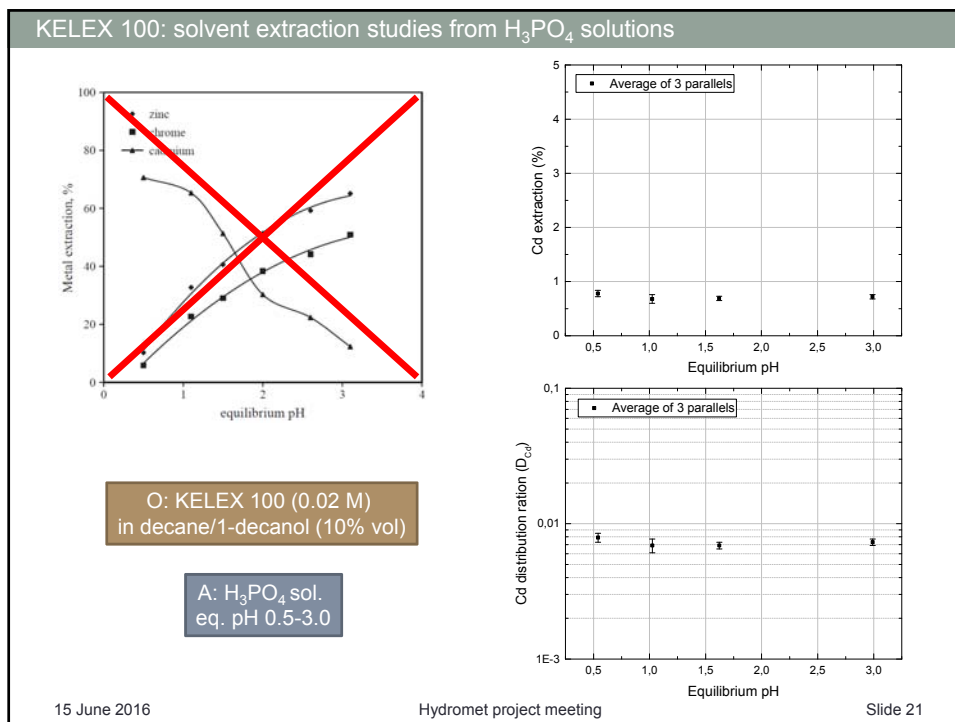
A: $\text{HNO}_3/\text{H}_3\text{PO}_4$ sol.
eq. pH 0.5-8.5



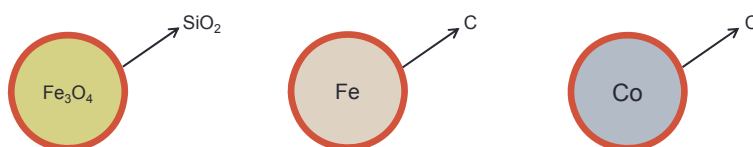
Z. Marczenko, M. Balcerzak, Separation, Preconcentration and Spectrophotometry in Inorganic Analysis (2000), 1st ed., Elsevier
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Magnetic particles: stability tests in Yara's mother liquors



Average dimensions of the magnetic cores: < 100 nm

Characteristics of synthetic mother liquor

Acids to be used	Concentration (%)	
%HNO ₃	65	xx
%H ₃ PO ₄	85	yy
%H ₂ SiF ₆	25	nn

Added together to become mother liquor	(%)	Weight (g)
HNO ₃ (xx%)	28,384	70,960
H ₃ PO ₄ (yy%)	33,759	84,397
Ca(NO ₃) ₂ ·4H ₂ O	26,715	66,787
H ₂ O	1,972	4,931
H ₂ SiF ₆ (nn%)	9,170	22,925
Sum	100,000	250,000

Characteristics of industrial mother liquor

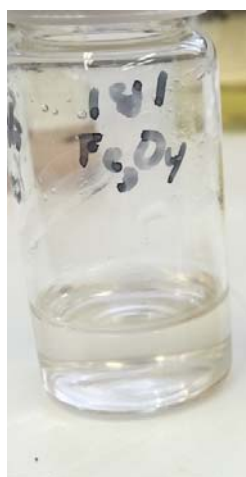
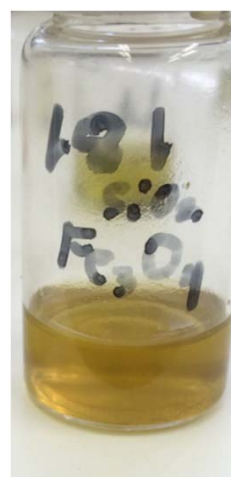
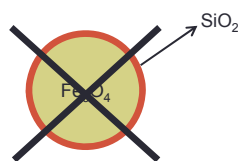
Acids	Concentration (%)
%HNO ₃	14
%H ₃ PO ₄	26

Relevant elements	Concentration (%)
%F	0.24
%Ca	3.7

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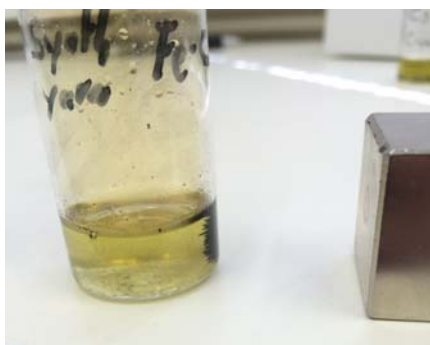
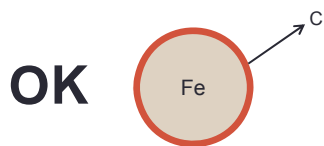
Stability tests of Fe₃O₄-SiO₂ particles24h residence
in synthetic mother liquor24h residence
in industrial mother liquor

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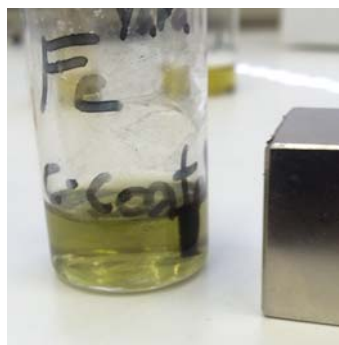
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Stability tests of Fe-C particles



24h residence
in synthetic mother liquor



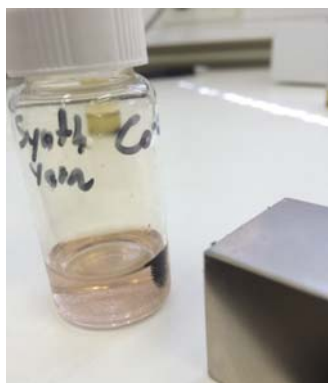
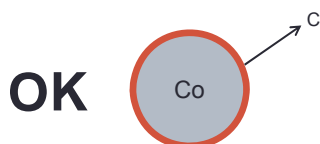
24h residence
in industrial mother liquor

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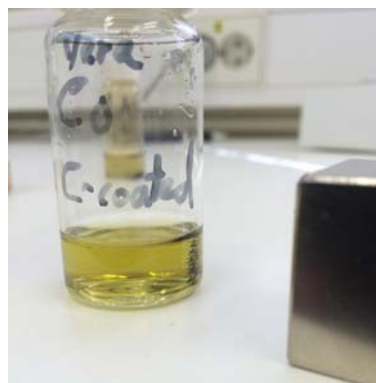
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Stability tests of Co-C particles



24h residence
in synthetic mother liquor




24h residence
in industrial mother liquor

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ICP-OES analysis of Yara's industrial mother liquor



}	Al	~ hundreds of ppm	D500
	Fe		
	K		
	Mg		
	Na		
	Cr	~ tens of ppm	D100
	Si		
	U		
	V		
	Zn		
	Cu	~ few ppm	D10
	Cd		
	Ni		
	Pb		
	Th		

1) Suitable emission lines → free from spectral interferences → 2-3 for each element → quality control

2) Three multielemental standard solutions + blanks (D500, D100, D10) → matrix matching

Acids	Concentration (%)	Relevant elements	Concentration (%)	
%HNO ₃	14	%F	0.24	→ H ₂ SiF ₆ (%)
%H ₃ PO ₄	26			

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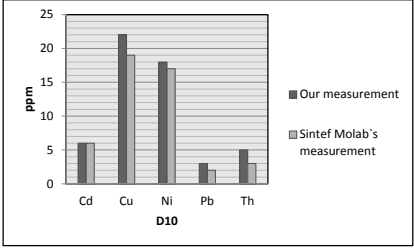
ICP-OES analysis of Yara's mother liquor

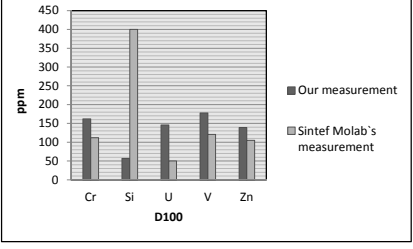
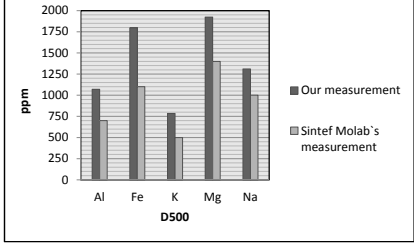
ELEMENT	λ (nm)	CONC. (ppm)
K	766,491	782,0
	769,897	787,0
Cr	205,560	162,1
	206,158	162,3
	267,716	161,8
Ni	216,555	17,5
	221,648	17,4
	231,604	18,0
Cd	214,439	6,4
	226,502	6,5

D500

D100

D10



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Summary

- The Odda process → Cd to be removed after crystallization step
- Bibliographic research → KELEX 100 & ammonium pyrrolidine dithiocarbamate as possible extractants
- KELEX 100 → chemically unstable in acidic $\text{HNO}_3/\text{H}_3\text{PO}_4$ environments
- KELEX 100 → not suitable for extraction in the pH range of interest (pH <1)
- Magnetic particles:
 - $\text{Fe}_3\text{O}_4\text{-SiO}_2$ particles dissolve in synthetic and industrial mother liquors
 - Fe & Co-C particles don't dissolve in synthetic and industrial mother liquors
- ICP-OES analysis of Yara's industrial mother liquor:
 - development of an analytical method
 - reproducible and comparable results for diluted elements (including Cd)

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Acknowledgements

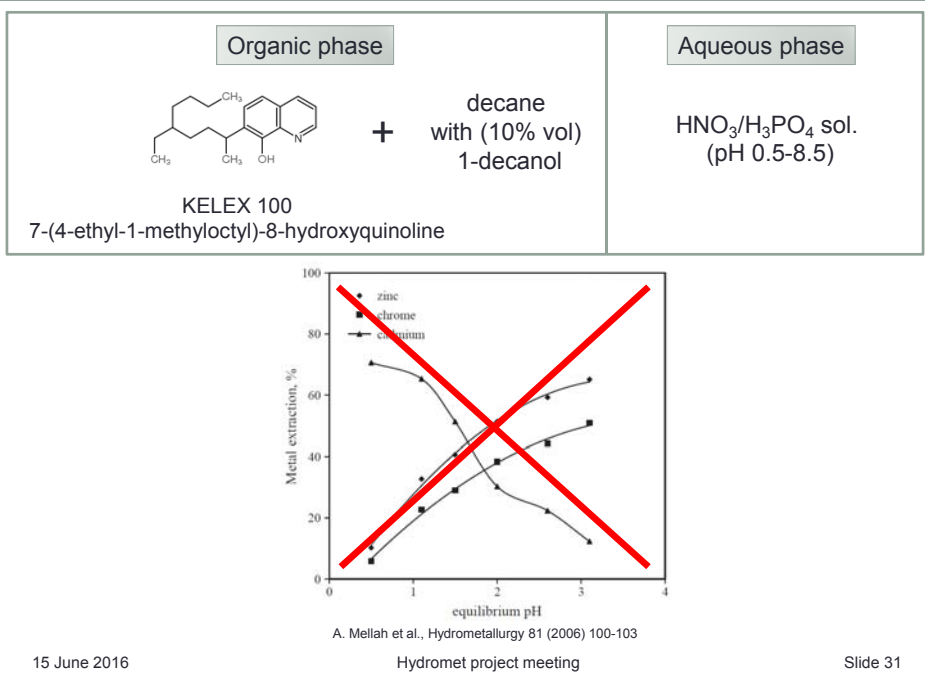
Thank you for your attention!

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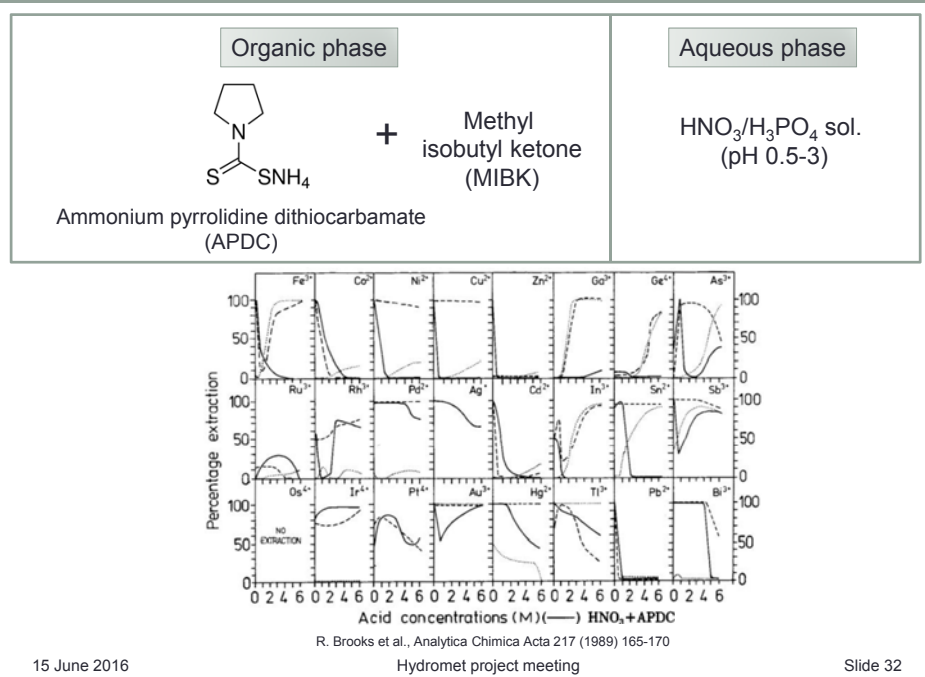
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Future steps: KELEX 100 further investigations & results publication



Future steps: ammonium pyrrolidine dithiocarbamate extraction tests



Future steps: a possible alternative...

Elemental sulphur: waste of the oil industry

SEPARATION, e.g., FILTRATION

Cd free

Cd

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Derivatives of KELEX 100 taken into account

5-chloro-8-quinolinol

5,7-dichloro-8-quinolinol

KELEX 100
7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline

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KELEX 100: solvent extraction studies from mixed HNO₃/H₃PO₄ solutions

HNO ₃ conc. (mol/L)	H ₃ PO ₄ conc. (mol/L)	μl addition of conc. (28%) NH ₃ liq.	pH before extraction	pH after extraction	Δ pH
0,3	0,3	NO	0,5	0,5	0
0,1	0,1	NO	0,9	0,8	-0,1
0,03	0,03	NO	1,4	1,4	0
0,01	0,01	NO	1,9	1,9	0
0,003	0,003	NO	2,5	2,5	0
0,003	0,003	YES	3,6	5,4	1,7
0,003	0,003	YES	4,2	5,6	1,4
0,003	0,003	YES	5,5	6,5	1
0,003	0,003	YES	6,7	6,8	0,1
0,003	0,003	YES	7,5	7,4	-0,1
0,003	0,003	YES	8,6	8,4	-0,2

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KELEX 100: solvent extraction studies from H₃PO₄ solutions

H ₃ PO ₄ conc. (mol/L)	μl addition of conc. (28%) NH ₃ liq.	pH before extraction	pH after extraction	Δ pH
2,5	NO	0,5	0,5	0
0,5	NO	1,0	1,0	0
7,40E-02	NO	1,6	1,6	0
1,50E-03	NO	2,9	3	0,1

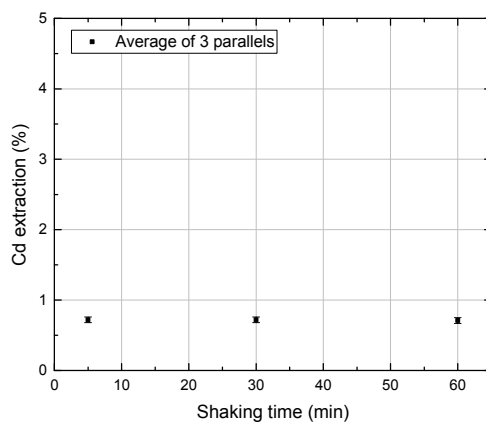
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KELEX 100: solvent extraction studies from mixed H_3PO_4 solutions

Equilibrium kinetics study



O: KELEX 100 (0.02 M)
in decane/1-decanol (10% vol)

A: H_3PO_4 sol.
eq. pH 2.99 ± 0.03

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