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Removing of cadmium ions from wet-process phosphoric acid using precipitation methods.

K. Borowik, P.Rusek, A.Bińczak, U.Ryszko
Łukasiewicz Research Network -New Chemical Syntheses Institute, Puławy, 24-110 Poland,
Presenting author email: krzysztof.borowik@ins.lukasiewicz.gov.pl

Wet phosphoric acid- crucial component for mineral fertilizers production

Phosphorus (P) takes its rightful place alongside Nitrogen and Potassium among the three primary macronutrients essential to successful plant growth.

Without phosphorus, photosynthesis could not occur. Phosphorus plays a key role in complex energy transformations that are necessary to all life, as a main ingredient in ATP (adenosine triphosphate). It is also a central component of DNA and RNA – and is necessary for building proteins and other compounds.

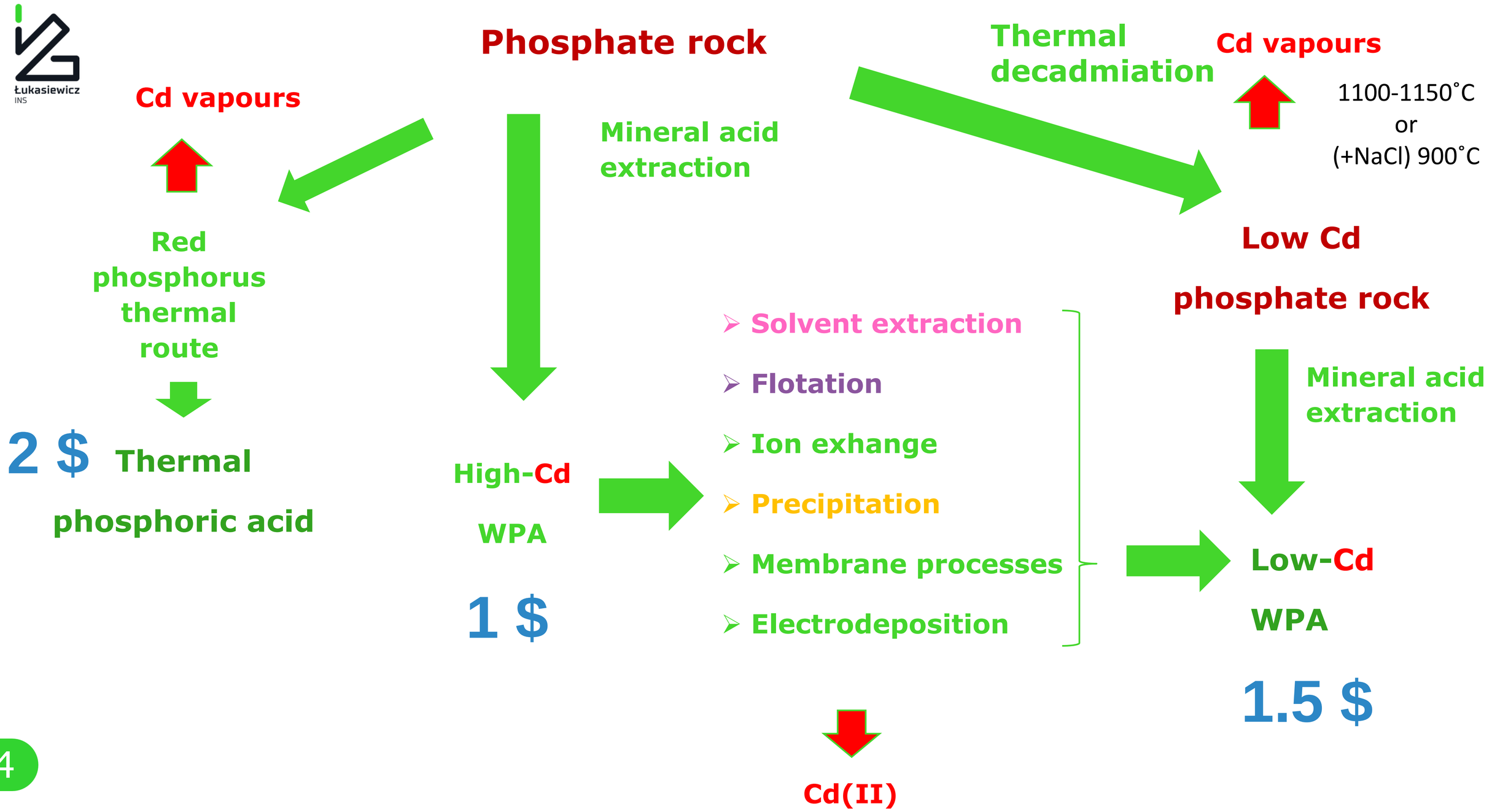
That is just the beginning. Phosphorus is required by the plant from the seedling stage through to maturity – and has a measurable impact on crop quality and yield.

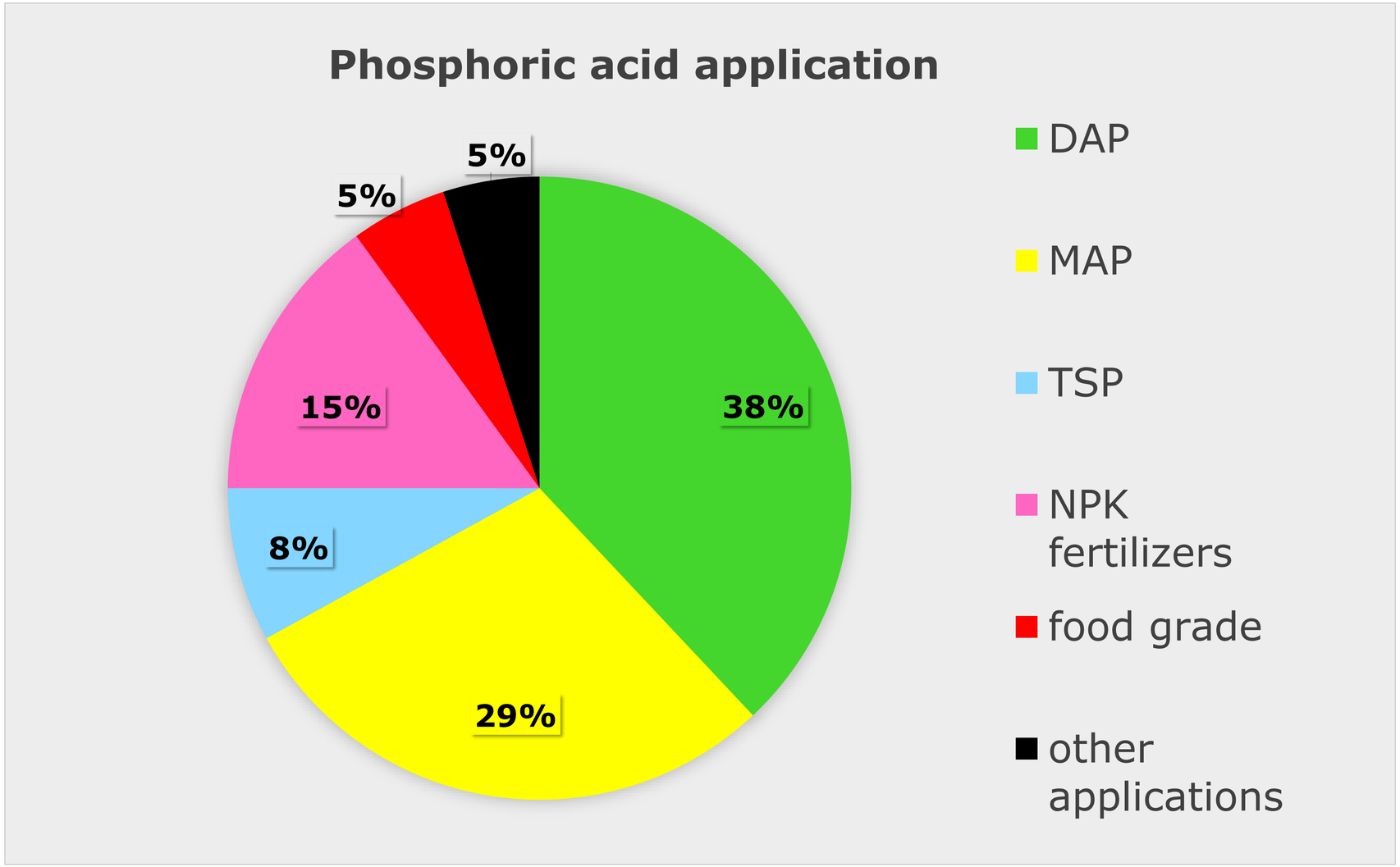
Typical composition of phosphate rock

P_2O_5	29-38%	U	100-200 ppm
Fe_2O_3	0.2-1%	Cd	<1-150 ppm
Al_2O_3	0.1-1%	REE	0.1-1%
CaO	48-52%	K	0.1-0.4
MgO	0.2-0.8%	F	3.3-4.3%
SiO_2	0.2-5%	Organic carbon	0-0.4 %

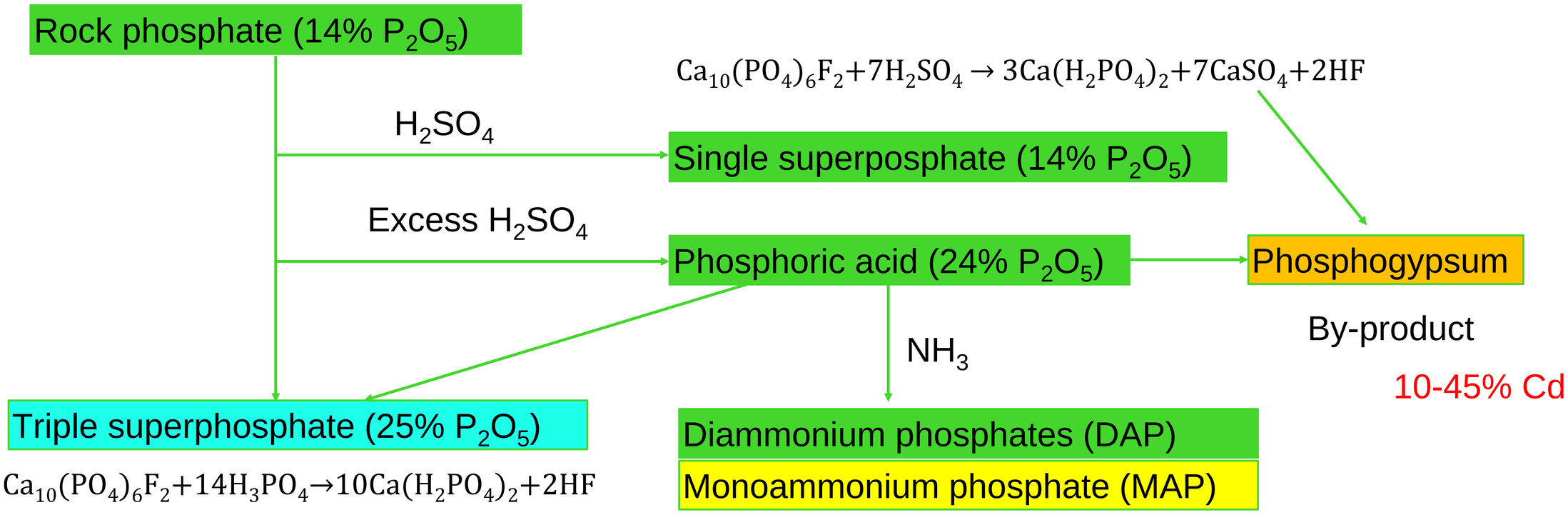
Global phosphate rock production in 2021 stood at 204 million tonnes (63 Mt P_2O_5) of marketable concentrate.

Phosphate rock resources technically recoverable reserves should last for more than **300** years.


Phosphate rock
Cd vapours
Red phosphorus thermal route
2 $
Thermal phosphoric acid
Mineral acid extraction
High-Cd WPA
1 $
Solvent extraction
Flotation
Ion exhange
Precipitation
Membrane processes
Electrodeposition
Cd(II)
Thermal decadmiation
Cd vapours
1100-1150˚C
or
(+NaCl) 900˚C
Low Cd phosphate rock
Mineral acid extraction
Low-Cd WPA
1.5 $

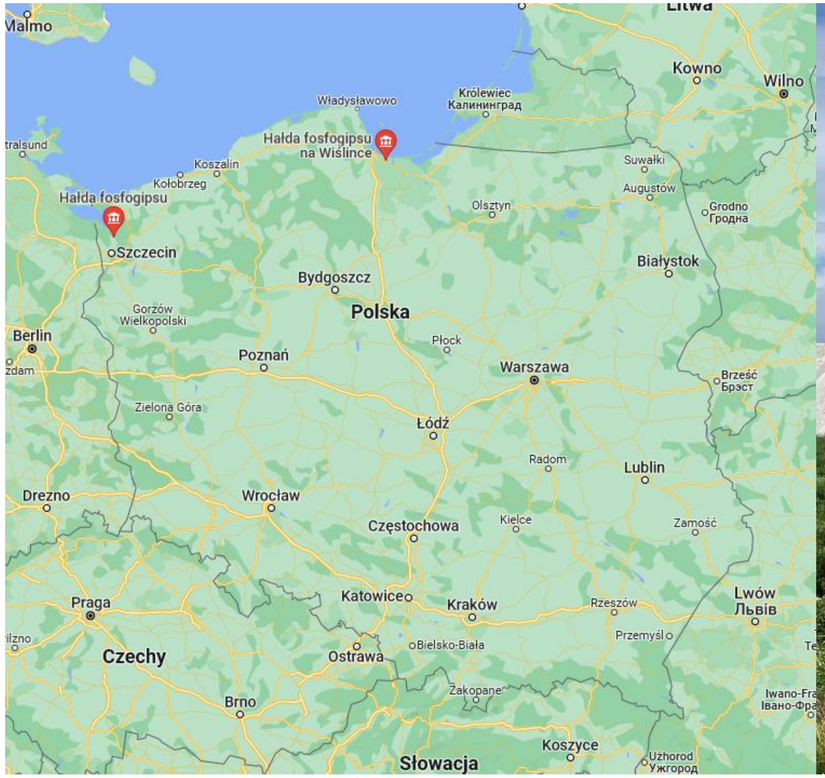

Phosphoric acid application
38%
29%
8%
15%
5%
5%
DAP
MAP
TSP
NPK fertilizers
food grade
other applications

Phosphate fertilizers production- wet route



Products 55-90% Cd

Phosphogypsum slag heap at Police



100 milion tonnes deposited, 2 milion tonnes/annually

Phosphogypsum slag heap at Wiślinka

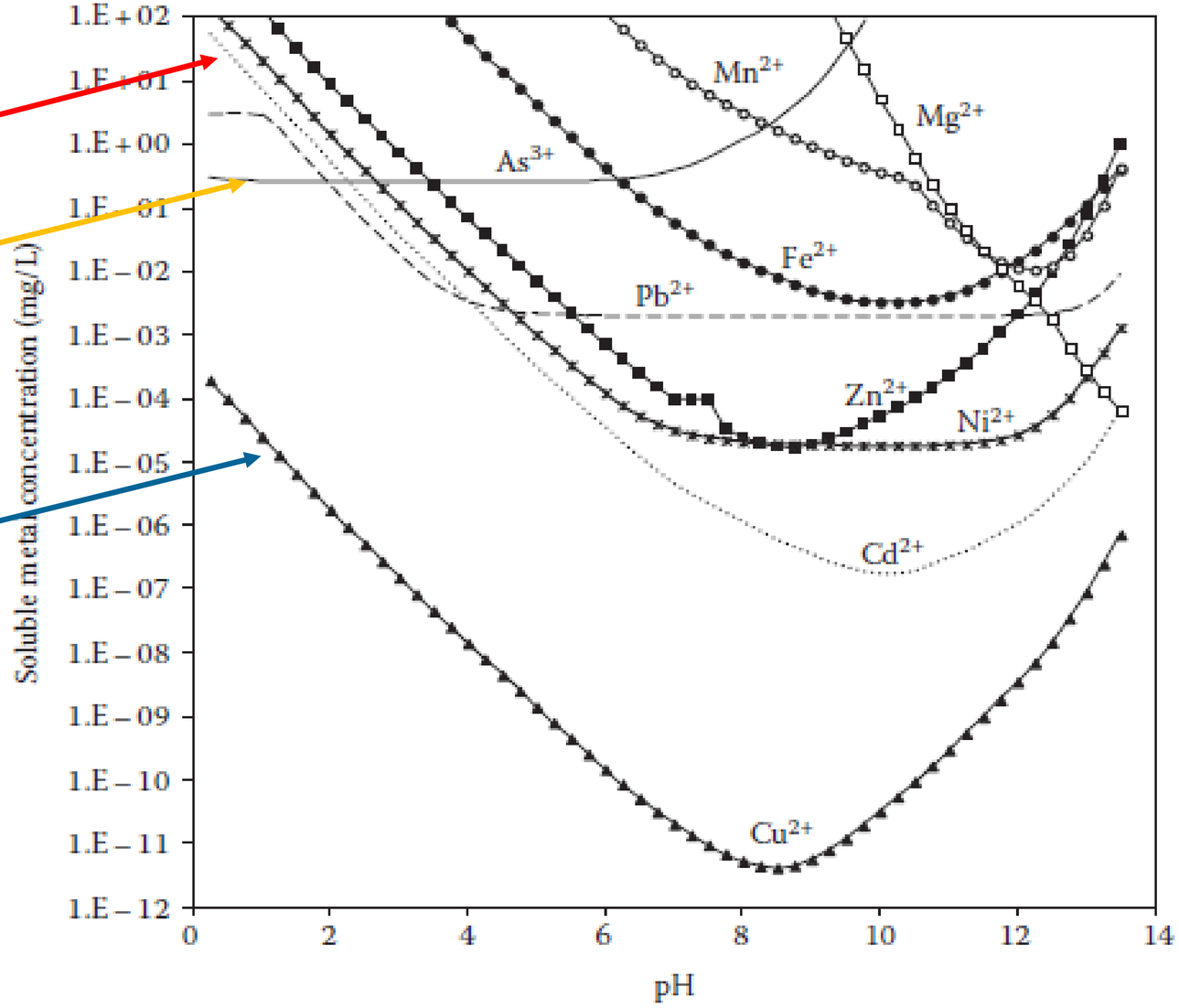
25 milion tonnes deposited

Metal sulfides solubility

Cd(II)

As(III)

Cu(II)



Elevated pressure
pH 0.9-1.5

https://upload.wikimedia.org/wikipedia/commons/0/0e/Cadmium_sulfide.jpg

$$Cd^{2+} + H_2S \rightleftharpoons CdS\downarrow + 2H^+$$

CdS precipitates partly from phosphoric acid at low pH. A higher degree of cadmium precipitation can be obtained after partial neutralization of the acid. Another way to increase the degree of precipitation of cadmium in the form of CdS is the reaction with hydrogen sulfide under elevaterd pressure e.g. (>5 bar, temp. 20 ^{o}C.). The efficiency of CdS precipitation decreases with increasing concentration of phosphoric acid from 10% to 30% P_2O_5 and with increasing temperature from 20 to 70 ^{o}C.

Other reagents which may be used for Cd precipitation:

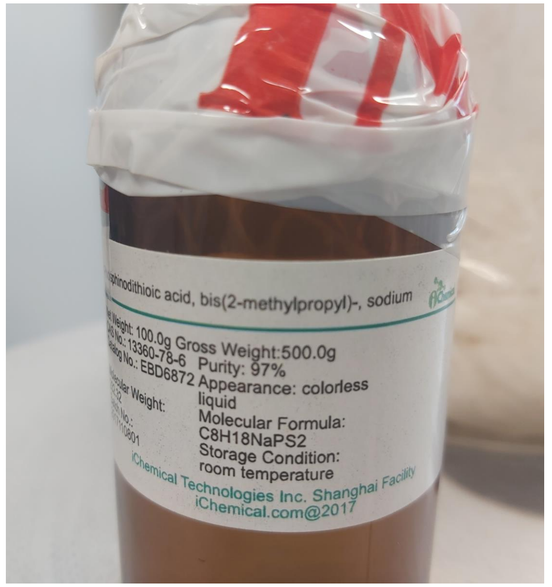
- sodium thiocarbonate, Na_2CS_3
- Sodium diethylodithiophosphate – $(CH_3CH_2O)_2PS_2Na$
- trimercaptotriazin, trisodium salt, $C_3N_3S_3Na_3$
- Sodium cellulose xanthate
- Sodium N,N-diphenyldithiocarbamate
- Sodium N-ethylophenylodithiokarbamate

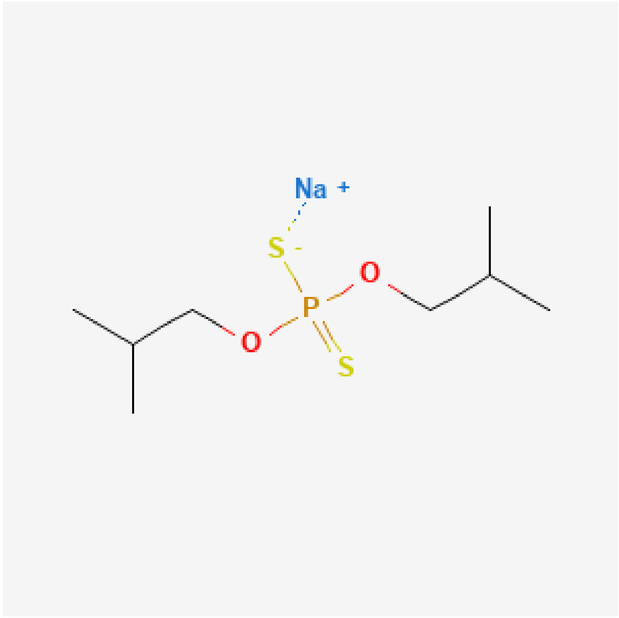
Reagents tested as Cd precipitation agents:

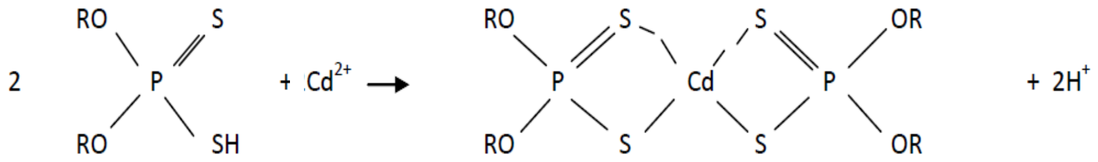
- DTPN - bis(2-methylpropyl)-phosphinodithioic acid sodium salt ($C_8H_{18}NaPS_2$)
- Cupral - Sodium diethyldithiocarbamate $(C_2H_5)_2NCSSNa \cdot 3H_2O$

Reactions Cd with DTPN

Phosphinodithioic acid, bis(2-methylpropyl)-, sodium salt ($C_8H_{18}NaPS_2$)
iChemical Technologies Inc. Shanghai Facility (China).







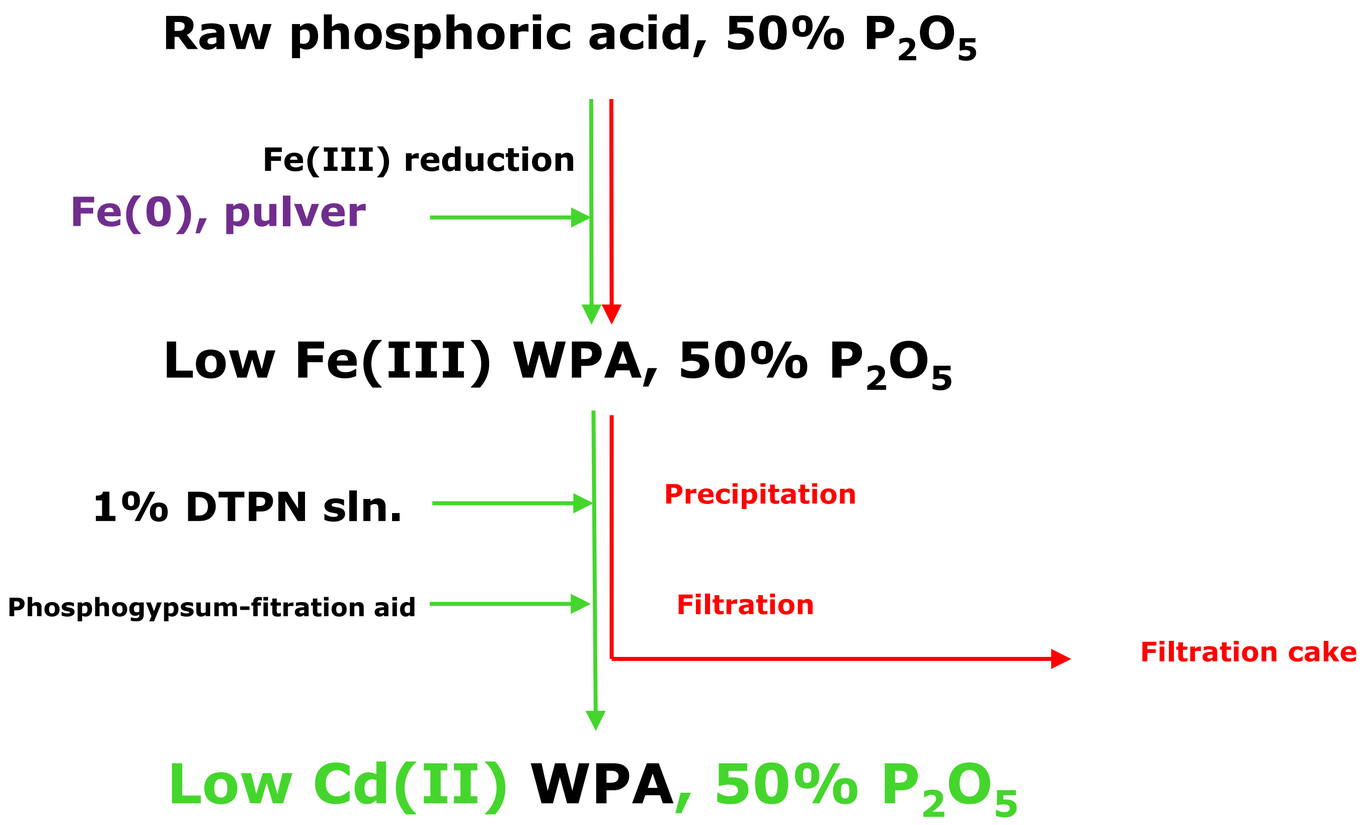
R = alkyl group C_4 –C_{10}

Main interferents:

$2Fe^{3+} + 2\ DTPN^- \rightarrow 2Fe^{2+} + (DTPN)_2 \downarrow$

$Cu^{2+} + 2\ DTPN^- \rightarrow Cu(DTPN)_2 \downarrow$

Wet Phosphoric Acid - Cd removal



Cd determination: GF-AAS

Purified WPA paremeters Police Chemical Plant

Parametr	Value	Unit
density	1.578	g/cm^3
P_2O_5	49.58	% (w/w)
Fe	0.36	%(w/w)
Al	0.39	%(w/w)
Mg	0.15	%(w/w)
Cd	18.77	mg/dm^3
Cu	1.28	mg/dm^3

WPA preparation for the tests:
reduction with metallic iron powder:
- iron dose 40g/L WPA
- ambient temperatrure ca.+25 ^{o}C
- contact time: 30min
- intensive stirring (600rpm)

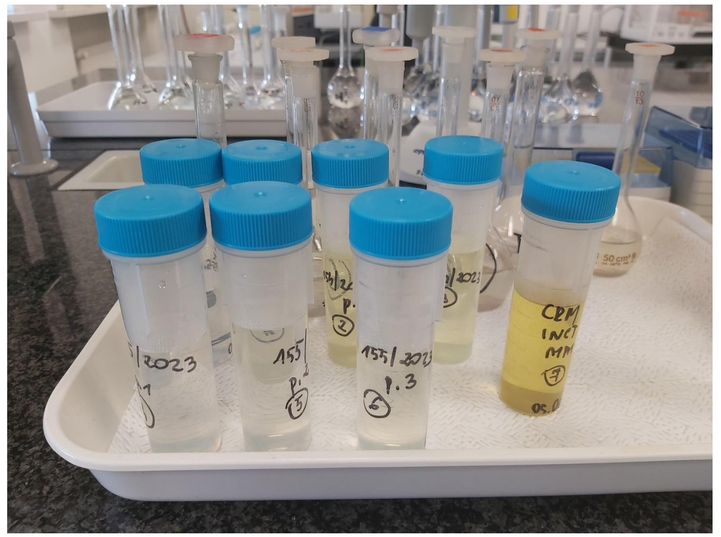
$Cu^{2+} + Fe^{0} \rightarrow Cu^{0} + Fe^{2+}$ **Cu(II) decerease from 1.28 to 0.11 mg/l**

$Fe^{0} + 2Fe^{3+} \rightarrow 3Fe^{2+}$ **total Fe incerease from 0.36 to 0.56 %**

Test procedure

Parameter	Quantity/Value	Unit
WPA	25	mL
DTPN concentration	1	g/100mL
DTPN volume added	0, 25, 50, 100, 250, 500	µL
Shaking time ($2min^{-1}$)	1	h
Temperature	20, 40, 60, 80	˚C

- Phase seperation- vacume filtration on 0,45µm nitrocelulose filter
- 2 g phosphogypsum as filtration aid
- Dissolution up to 50 ml



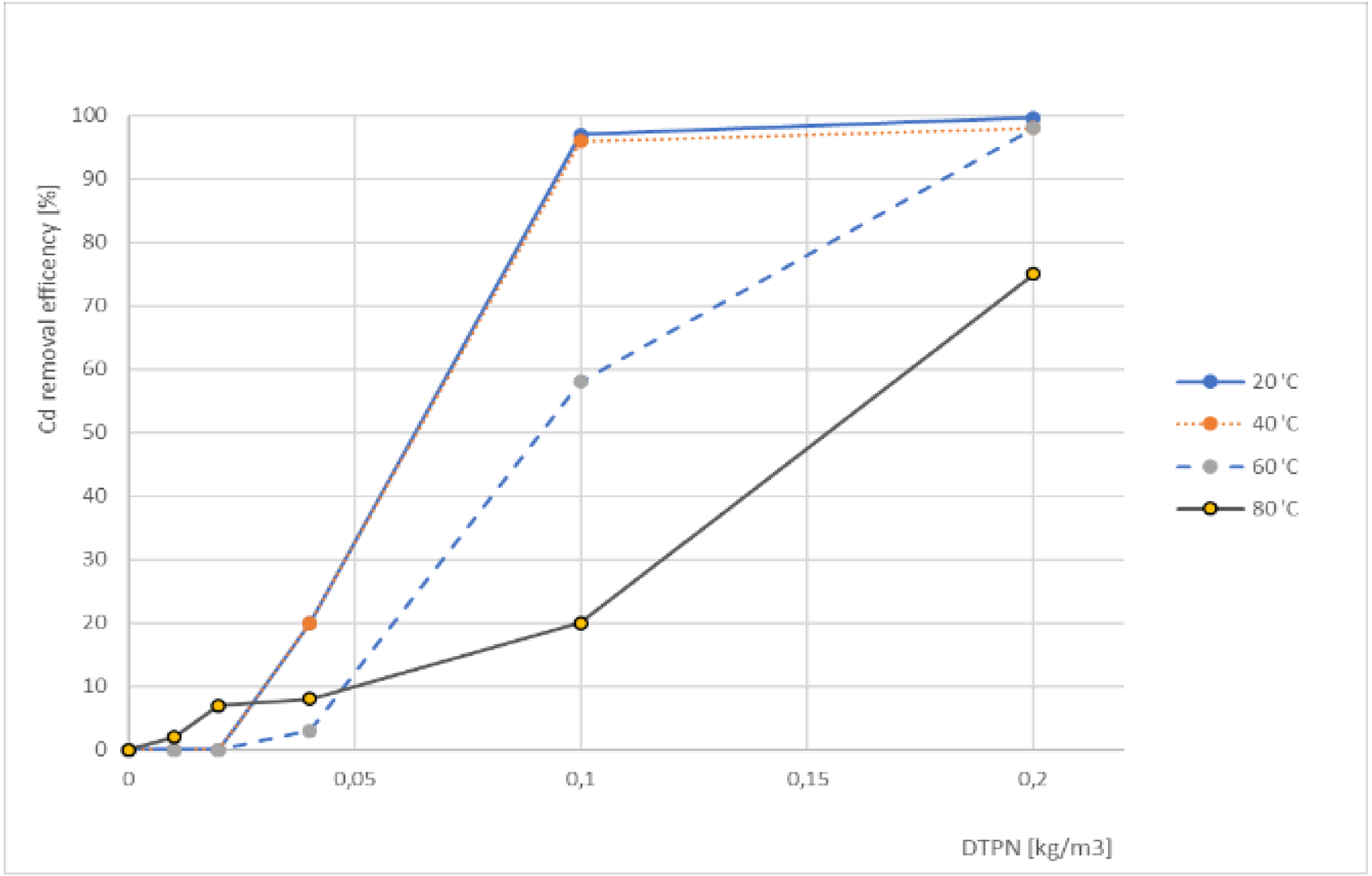
Analytical procedure

Cd determination in liquid phase: GF-AAS AA240Z/GTA120 VARIAN

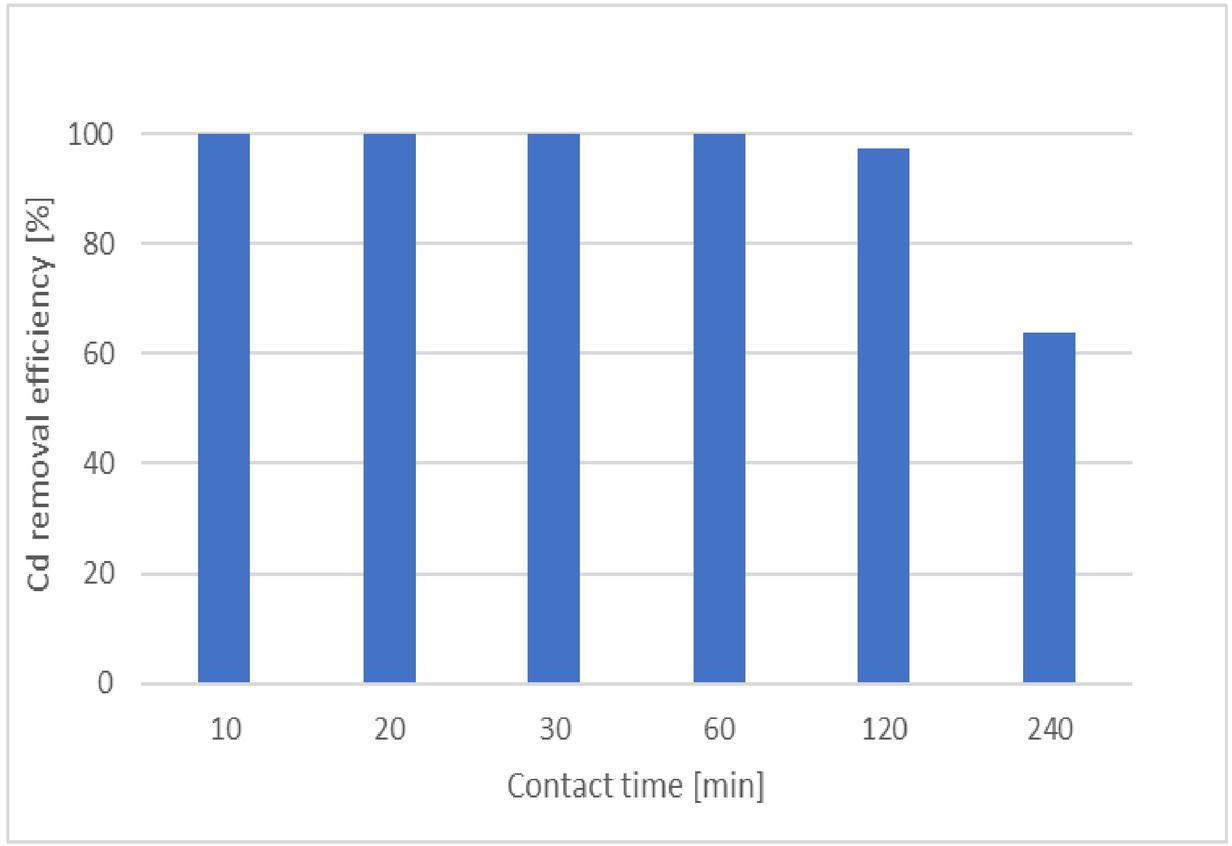
Parameter	Cd
Backgrund correction	Zeeman
Calibration mode	peak height
Wavelength [nm]	228.8
HKL current [mA]	4,0
Matrix modifier	1% $NH_4H_2PO_4$
Calibration curve	0.5; 1.0; 1.5 µg/l

LOD > 0.05 mg Cd/L

Influence of temperature and DTPN on Cd removal efficiency from WPA



Influence of reaction time on Cd removal efficiency from WPA

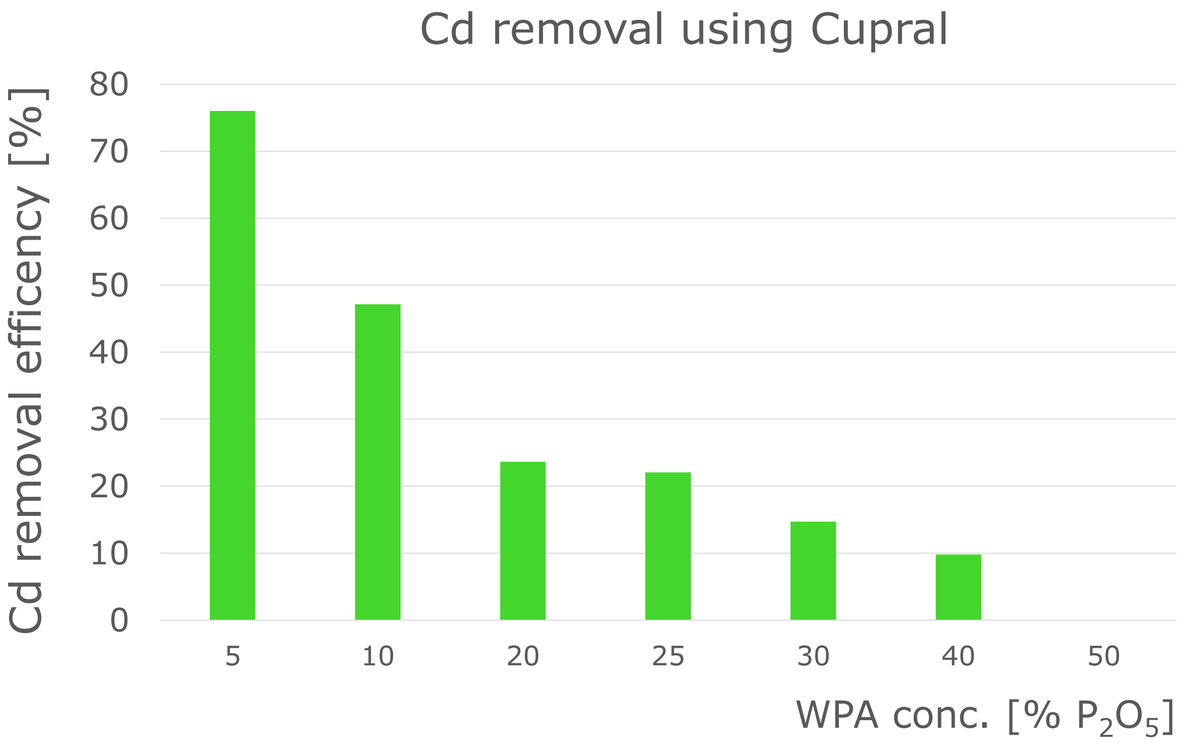


Experiment conditions:

- **WPA volume: 25 mL**
- **DTPN: 0.20 g/L WPA**
- **Temperature: ambient**
- **Phase contact time: 1h**
- **Filtration with 1g of phosphogypsum as filtration aid**
- **Flushing with water, volume up to 50 mL**

Cupral - Sodium diethyldithiocarbamate trihydrate

$(C_2H_5)_2NCSSNa \cdot 3H_2O$



Experiment conditions:

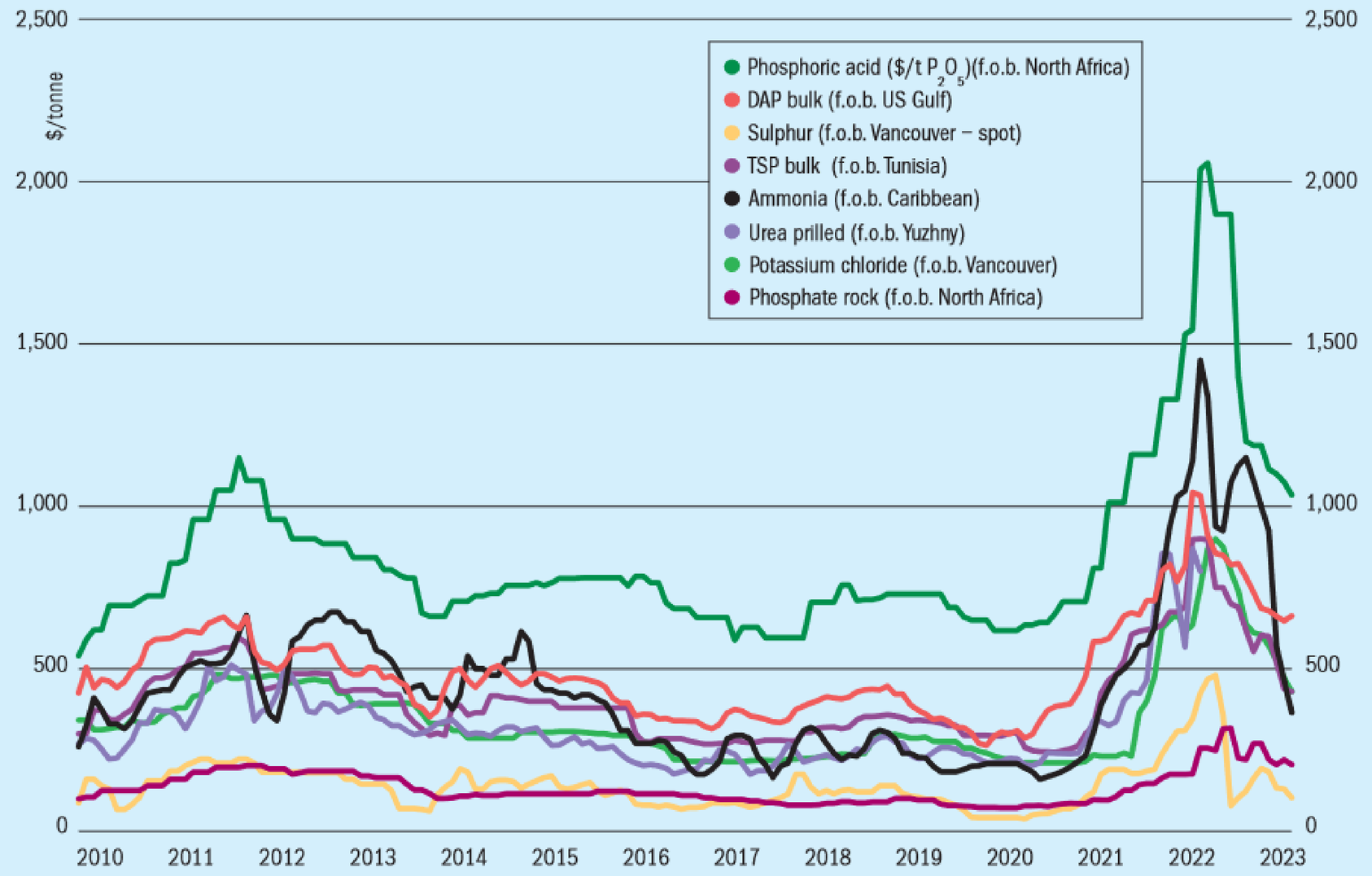
- **WPA no prior preparation,**
- **WPA volumume: 25 mL**
- **Cupral: 0.500 g (L:S=50)**
- **Temperaure: ambient**
- **Phase contact time: 2h**
- **Filtration with phosphogypsum as filtration aid**

Conclusions

Optimal parameters of cadmium removal:

- **DTPN is effective in Cd removal at concentrated acid solution;**
- **phosphoric acid reduction with metallic iron at ambient temperature;**
- **cadmium precipitation at ambient temperature;**
- **contact time: less than 60 min;**
- **filtration with phosphogypsum as filtration aid;**
- **minimal DTPN consumption 0.1 kg/1m^3 WPA;**
- **cadmium removal efficency >99.5% (to less than 1 mg/L)**
- **High cost of the DTPN reagent**

Historical price trends $/tonne



Source: BCInsight

Thank you for your attention

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