SeeWay-project
Novel methods to remove metal ions from waste water in 0.1 l – 100 m^3 scale

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SEEWAY-project

* Smart Metal Recovery and Water Treatment Systems
* Part of Green Maining program
* Funding period for 1.1.2013 – 31.3.2015
* Aim: demonstrate smart water systems which have capabilities to recover metals in low-concentration mine water streams also in the exceptional situations
* Based on multidisciplinary networking between geochemistry, chemistry, informatics, water-engineering and energy research

Partners: Geological Survey of Finland (GTK), University of Eastern Finland (UEF), University of Oulu, Savonia University of Applied Sciences, 7 Companies

MineWaCon-project

* Mobile Research Environment for Mine Waters
* Part of Green Maining program
* Funding period 1.1.2013 – 31.12.2013
* Aim: 1) create infrastructure for SEEWAY-project; 2) build up portable and adaptive purification container
* Pilot systems are tailored with modules of the measurement, online-analytics, automation and process units

Partners: Geological Survey of Finland (GTK), University of Eastern Finland (UEF), Savonia University of Applied Sciences, Several companies

UEF Spearhead

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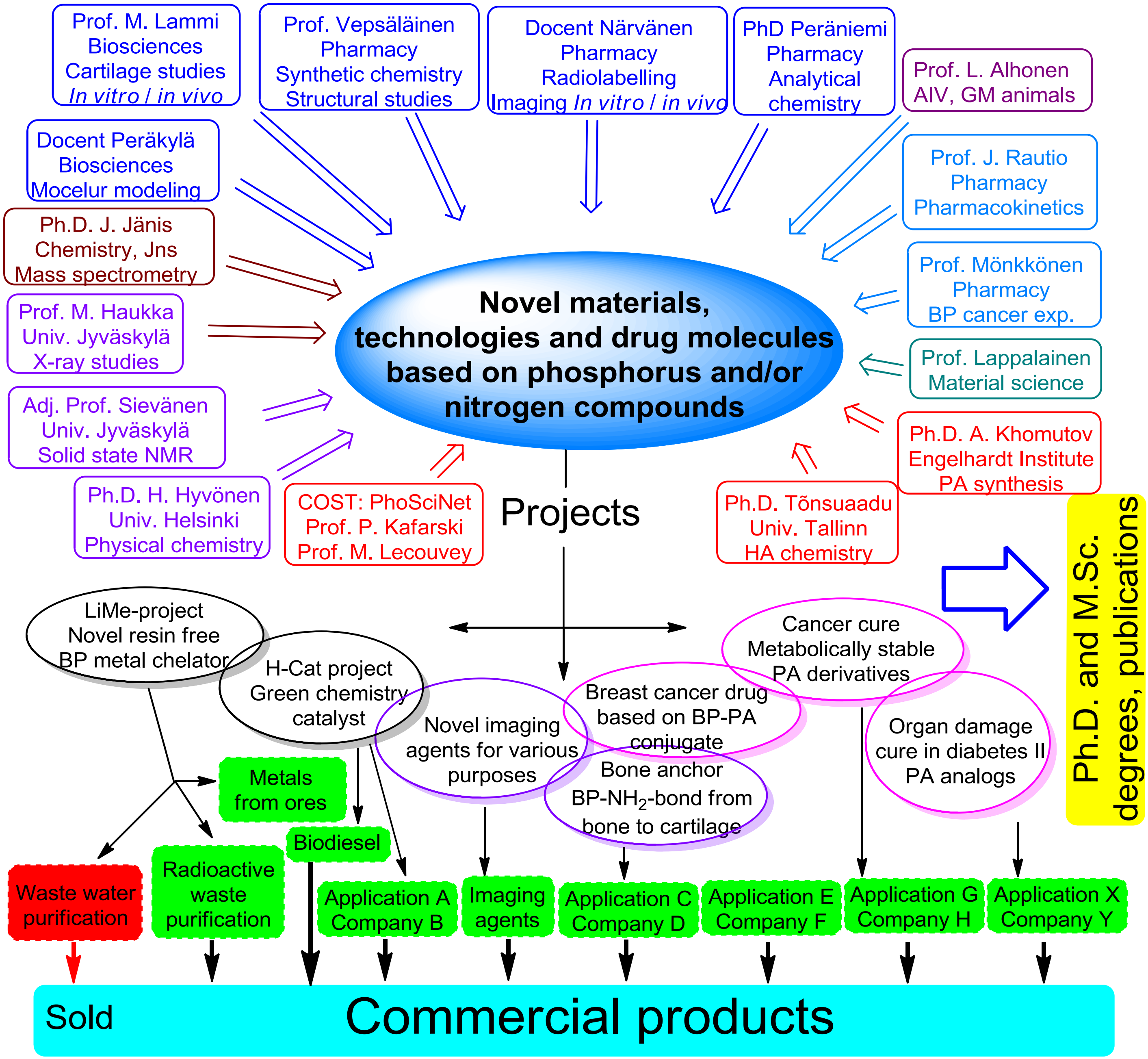

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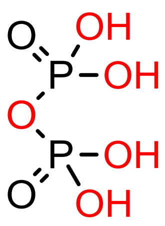
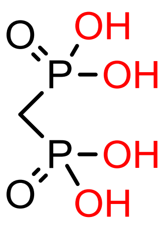
Introduction to bisphosphonates

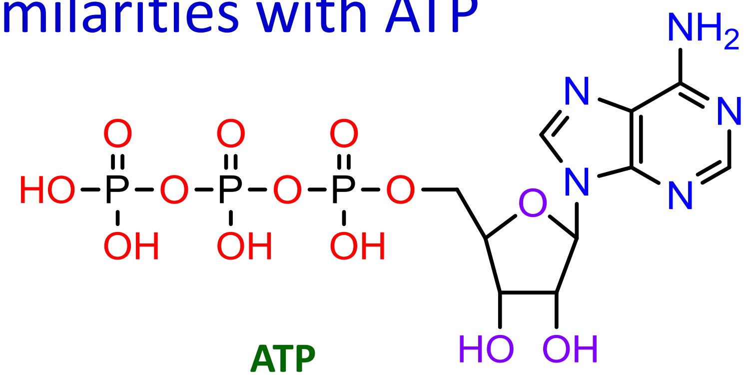
- bisphosphonates (BPs) are analogues of naturally occuring pyrophosphates, P-O-P
- they also have structural similarities with ATP



Pyrophosphate



Bisphosphonate

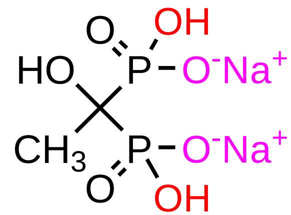


ATP

- the first BP was prepared on 1860s
- BPs as bone targeting agents were discovered late 1960’s
- nowadays ca. 15 BPs are in clinical use

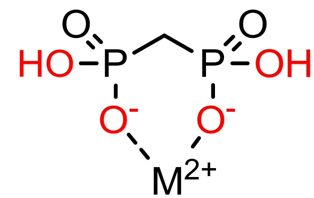
Properties of BPs

- BPs are highly acidic and ionic compounds

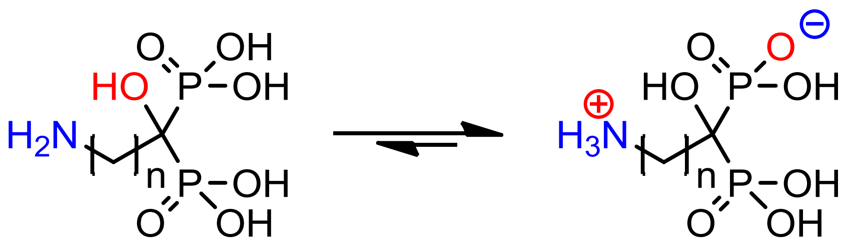


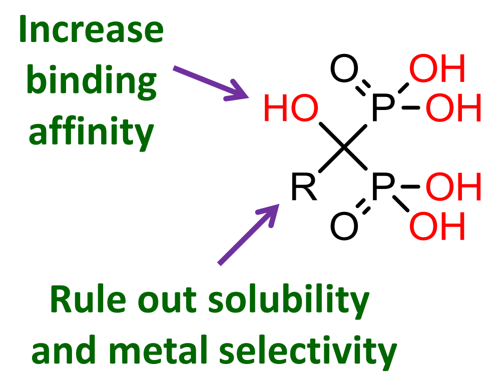
pK_a 1.9
2.8
6.8
10.2

- BPs are good chelators for various metal cations like Ca^{2+}



- amino-BPs are used as bone drugs





- generally properties of BPs are depending on the group R
- nowadays ca. 30 000 BPs are known

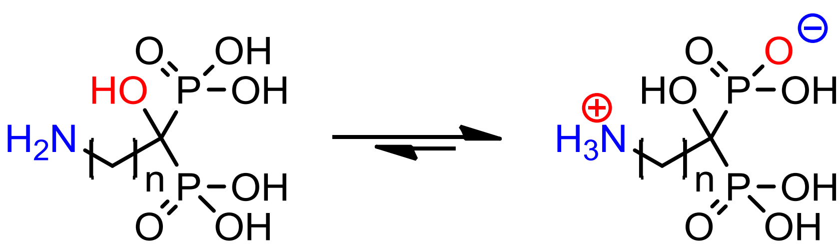
BP applications

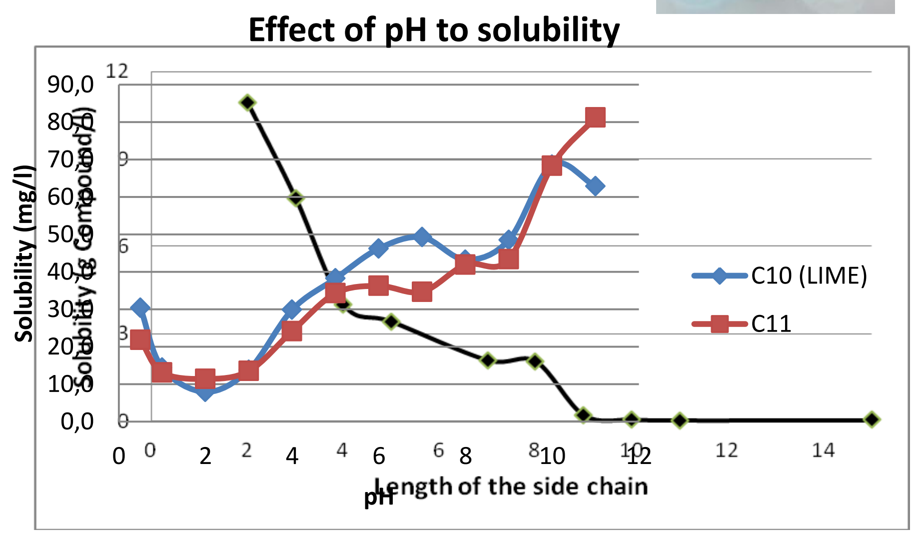
- in the beginning BPs were used as water softeners
- typical examples of medical use are antitumor agents, drug delivery agents, radiopharmaceuticals, anti-inflammatory agents, …
- in agriculture as fertilizers and in food science (etidronic acid) as anti-oxidant
- in metallurgy as surfactants for metals, scale inhibitors, corrosion inhibitors, …
- in chemistry as chelating agents, catalysts, …
- in polymer chemistry as modifiers and additives
- in environmental chemistry as waste water purification agents

BPs as metal dragnet (N10O)

Target: Develop novel resin-free ion exchange materials for metal chelating

- ídea is based on a sparingly soluble BP derivative N10O (LiMe)
- while N10O is solid it still adsorb metal ions from solution effectively
- solubility is chain lenght and pH dependent





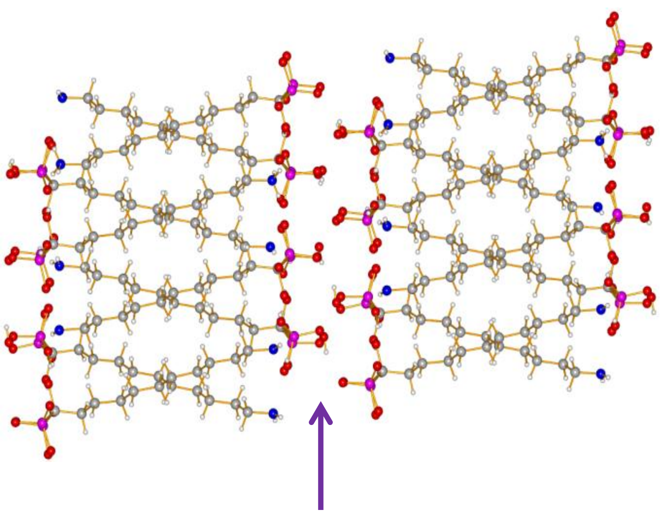
Quantitative analysis BPs

- no direct method to analyze solid BPs quantitatively
- general spectrophotometric method developed based on "Molybdenum Blue" method
  - BPs are decomposed to orthophosphates under microwave digestion with a strong acid (e.g. HNO_3)
  - phosphate ions form under acidic medium intensively blue complex with ammonium molybdate which is measured at 880 nm wavelength

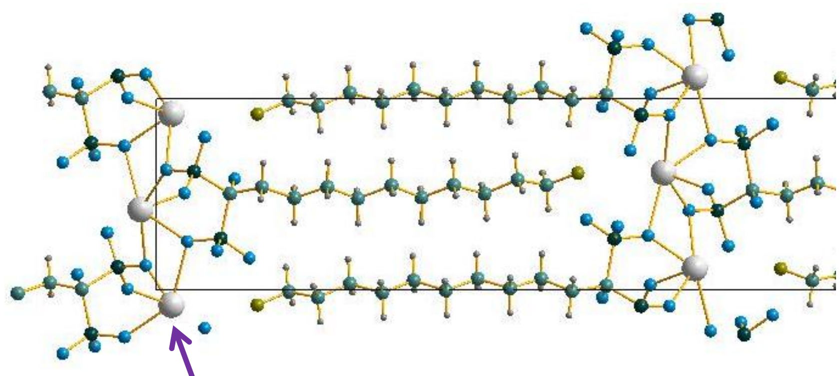
- applications:
  - elemental analysis of phosphorus
  - BP quantification from liquids and solubility determination
  - quantification of bounded BP on different types of resins or particles
  - limitation: not for compounds containing already phosphorus

Mechanism of action

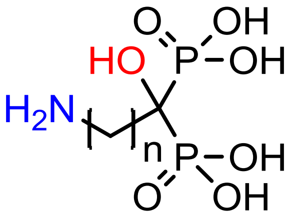
- somehow behavior resembles commercially available resins like Diphonix (these are 10x more expensive)
- N10O is formed from microcrystals (30 x 50 x 5 μm)
- there is no need for additional resin
- inside the crystal there is ion chanels in which metal ions are collected



Ion chanel



Pb^{2+} cation inside ion chanel



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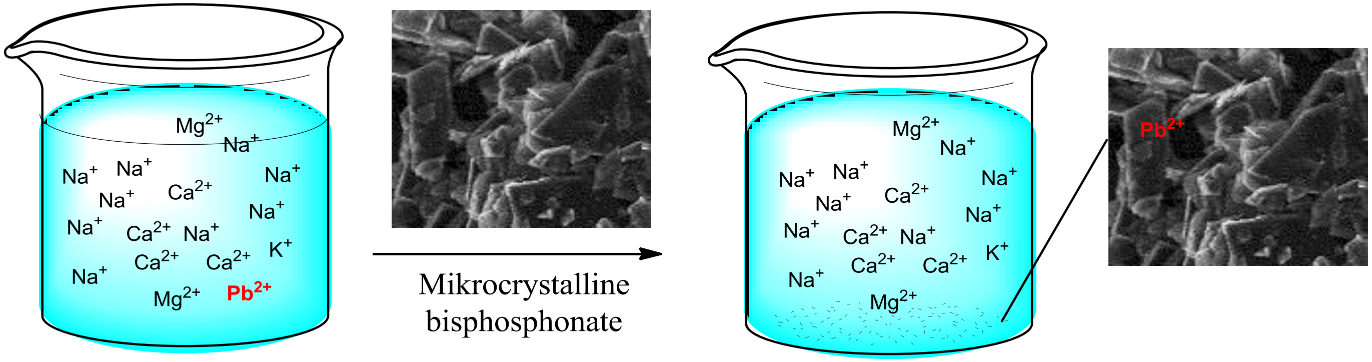
Traditional method

- traditionally metal ions are removed from solution by resipitation agent, e.g. EDTA
- after formation (coagulation) solids are filtered out
- several problems: 1) resipitation step might be slow, 2) good for concetrated solutions – poor in ppm scale, 3) have to have an idea of amounts of metals in solution, 4) recycling of complexation agent is almost impossible

Metal dragnet method

- in the case of **N10O** complexation agent is already solid
- no need for resipitation step - metal ions are moved from solutions directly inside microcrystalline bisphosphonate
- process is rather fast (2-10 minutes) and also small amounts (< ppm scale) are removed effectively
- regeneration of **N10O** is possible at least 20 times



Summary of toxicity

1) Acute toxicity in rat:
The purpose of this study was to investigate the acute toxicity of the test item KUC-24010, according to the OECD Fixed Dose procedure after single oral (p.o.) dose in the rat.

2) AMES Test:
The bacteria reversed mutation assay (Ames Test) was used to evaluate the mutagenic properties of the test item with five strain. The bacteria reversed mutation assay (Ames Test) was used to evaluate the mutagenic properties of the test item. Bacterial Reverse Mutation Test was conducted using *Salmonella typhimurium* tester strains viz. TA97a, TA 98, TA 100, TA 1535 and TA 102. This study was performed in full compliance with the OECD guidelines for testing of chemicals section 4, *Salmonella typhimurium* Reverse Mutation Assay, Test No.471 revised in December 1997.

3) Ecotoxicology
(a) Acute toxicity for *D. magna*: The purpose of acute toxicity test for *D. magna* test (SFS-EN ISO 6341; 1996) was to determine the median effective concentration for immobilization (EC50) of the test item to *D. magna* for 24 and 48 h. Test item (405,4 mg) was added to 1000 mL of reverse osmosis water. Suspension pH was 6,04 and oxygen conc. 8,7 mg/L. Lighting: 16/8 h (l/d), 1500 Lux, temp. 22 ± 1 °C. Suspension was diluted to water (3 parallel/conc., pH 7,7, cond. 49,6 mS/m) and *D. magna* (5/test tube, age <24 h) exposed by the test item.

Results

According to the present study results, the test item KUC-24010 has not observed any toxic effects in acute toxicity study in rat, Ames-test or ecotoxicological studies.

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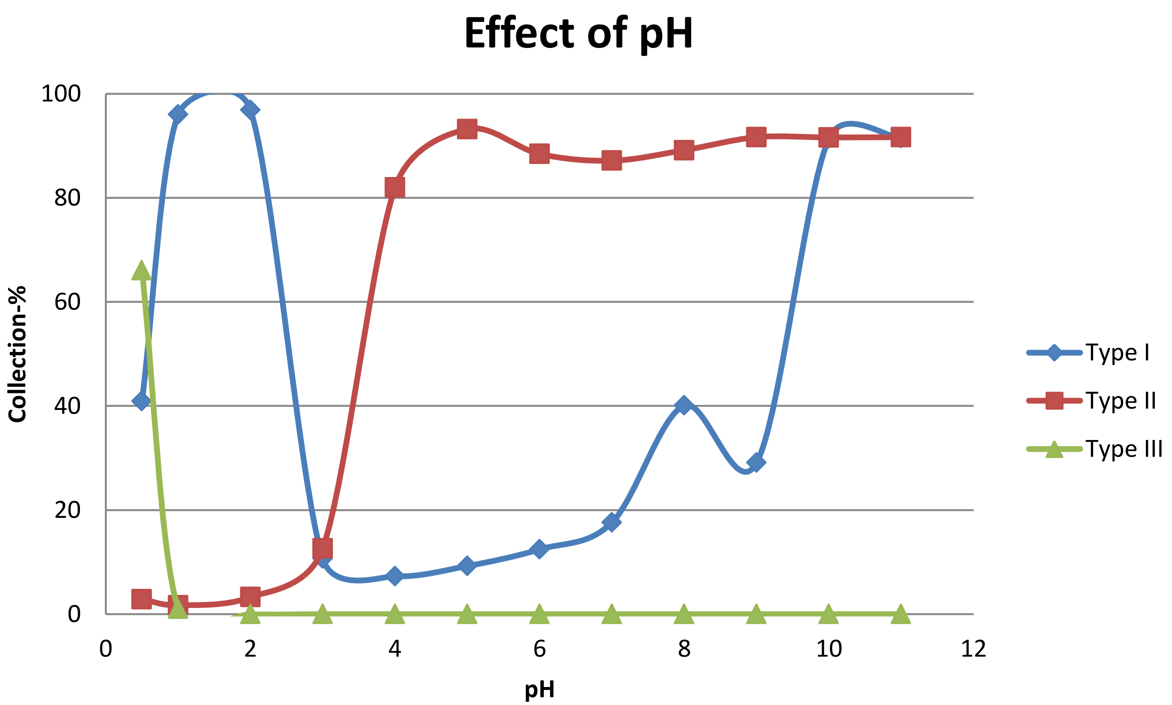
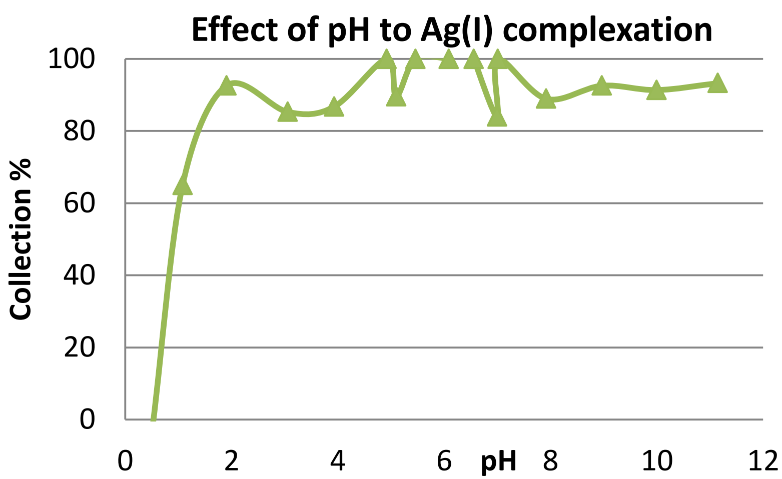
SBW Toxis In vivo Services

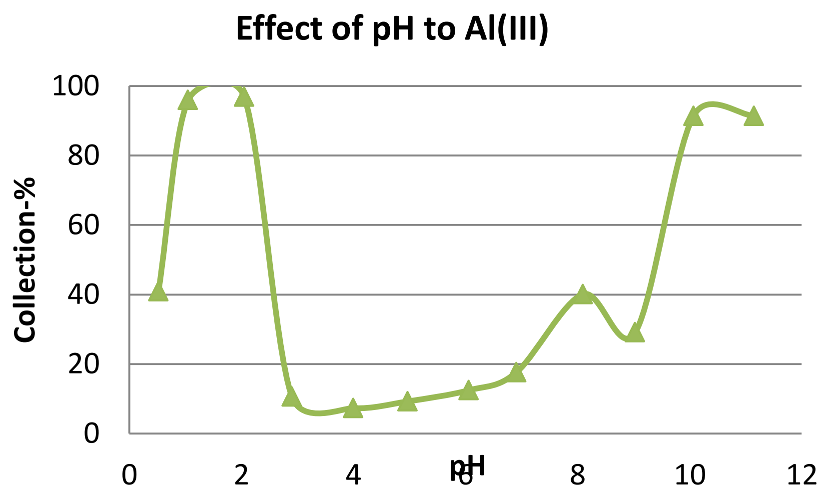
Complexation is pH dependent

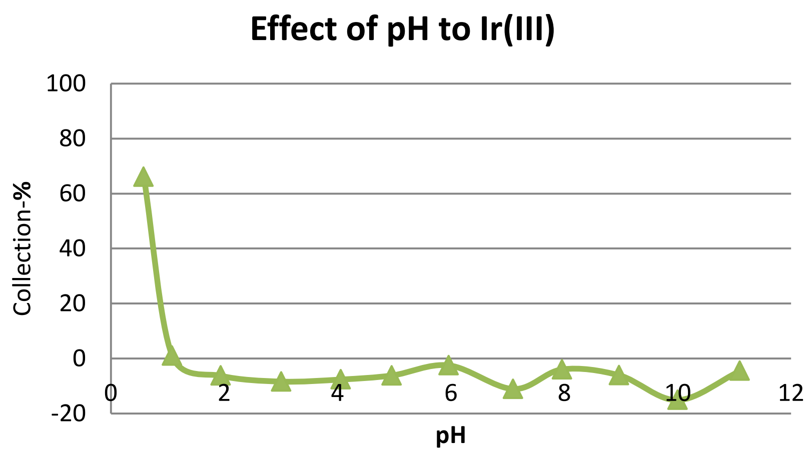
- complexation is pH and metal dependent:
- type I (e.g. Al) collection only on a sharp range)
- type II (e.g. Ag, Ni, Co, Pb,…) collection after a pH value
- type III (e.g. Ir) collection before a pH value

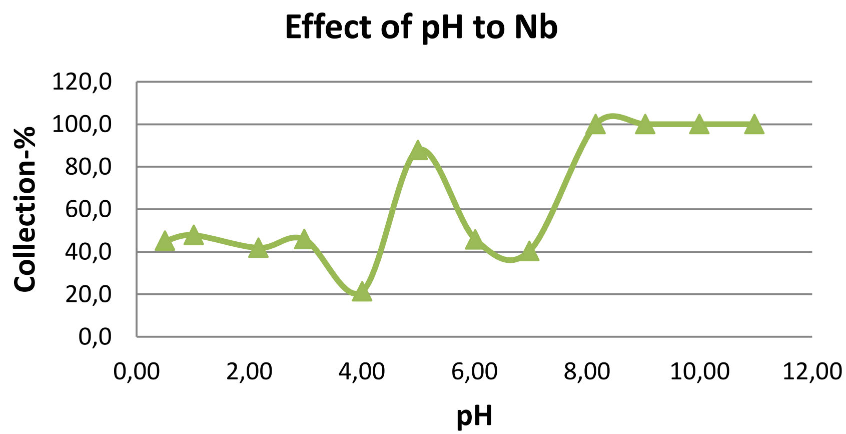


Complexation vs pH



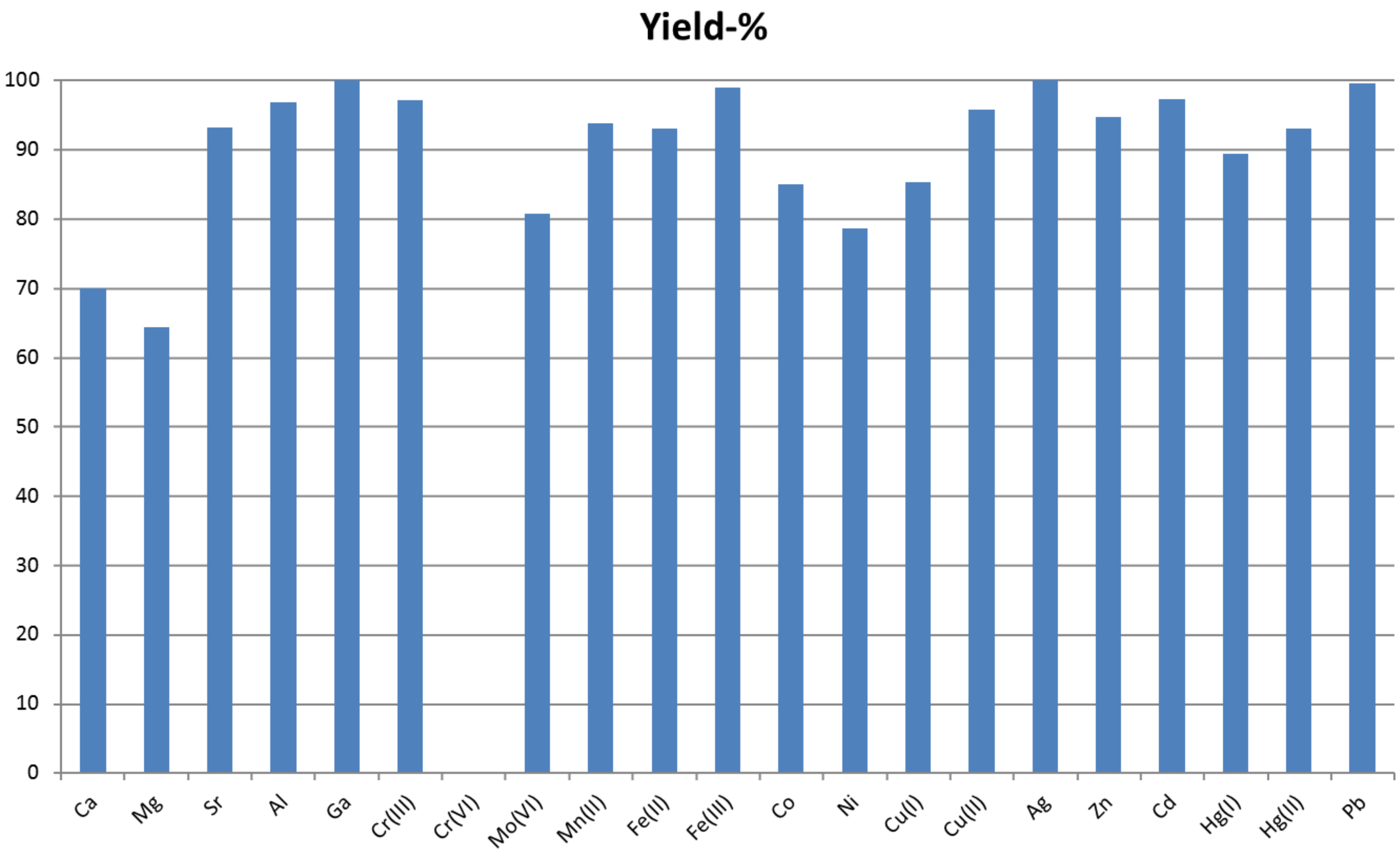






N10O and metal collection

- collection properties studied for ca. 50 elements



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N10O capacities

Element	pH	Cap. [mg/g]	Element	pH	Cap. [mg/g]
Ca^{2+}	4.0	50.9	Mo^{6+}	9.1	97.2
Cu^{2+}	4.0	61.6	Ag^{+}	2.5	94.6
Ni^{2+}	4.0	13.1	Co^{2+}	4.5	85.5
Zn^{2+}	4.0	70.9	**Cr^{3+}**	**3.5**	**1.0**
Au^{3+}	4.0	19.0	Fe^{2+}	3.0	82.7
Cd^{2+}	4.0	74.1	Fe^{3+}	3.0	15.2
Pb^{2+}	4.0	85.6	**Sc^{3+}**	**2.0**	**19.1**

- typically 2-5 N10O molecules is needed to bind one metal atom: Ca 46 %; Cu 35 %; Zn 40 %; Ag 32 %; Fe(II) 54 %; Fe(III) 10 %; Cr 1 %, Sc^{3+} 21 %

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Water purification

- artesian well from Tampere (DW1) and Turku (DW2)

Element	Al^{3+}	Ca^{2+}	Cu^{2+}	Mg^{2+}	Mn^{2+}	Na^{+}	Sr^{2+}	Zn^{2+}
Concentration	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**	**mg/l**
DW 1[1)]	<0.05	43,8	<0.05	10,9	0,095	15,2	**0,097**	**0,044**
After 1a[2)]	<0.05	0,232	<0.05	<0.1	<0.02	13,5	**<0.02**	**0,018**
Removal [%]	nd	**99**	nd	**99**	**79**	**11**	**79**	**59**
DW 2[3)]	0,107	22,2	**0,271**	13,60	<0.02	19,0	**0,113**	**0,284**
After 1a[2)]	<0.05	0,479	**<0.05**	0,102	<0.02	17,3	**0,029**	**0,026**
Removal [%]	**53**	**98**	**82**	**99**	nd	**9**	**74**	**91**

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Waste water purification

- drainage water purification from poluted soil

Element	Al^{3+}	Ba^{2+}	Ca^{2+}	Cd^{2+}	Mg^{2+}	Mn^{2+}	Mo^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
TS 1*	76	32	51	nd	81	>57[a]	58	50	nd	89
After addition of Cd ja Pb	67	26	48	>96[a]	78	>51[a]	52	33	>94[a]	90

*amount of metal (%) in solid LiMe, spiked metls are marked with red color, [a] minimum expulsion-%

- heavy element removal from Riihimäki sample

Element	$As^{3/5+}$	Ca^{2+}	Cd^{2+}	Cr^{3+}	$Fe^{2/3+}$	Pb^{2+}	Sr^{2+}	Zn^{2+}	$Hg^{1/2+}$
TS 2*	61,7[2)]	75,4	>89[a]	23,9	22,8	>69[a]	84,3	76,8	>99[a]

*amount of metal (%) in solid LiMe, [a] minimum expulsion-%

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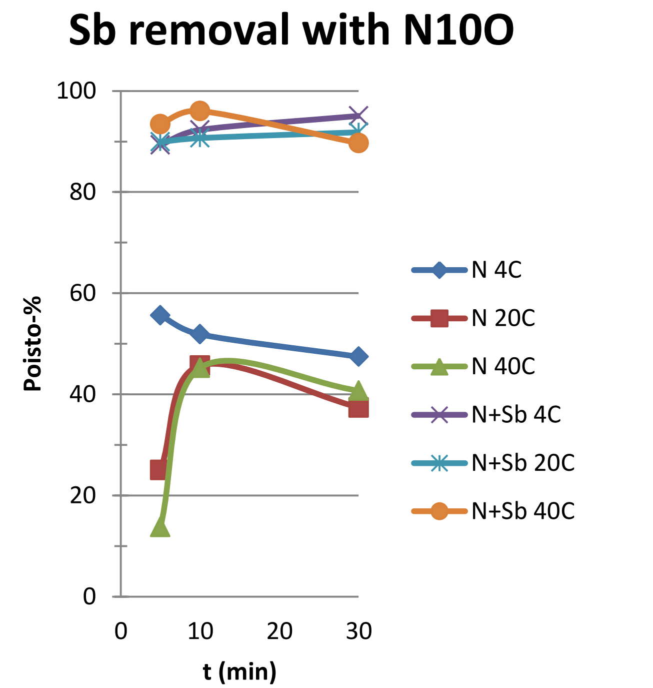
Remove of Sb and U

- antimony is common in some gold ores
- challenging to remove by traditional methods, especially in ppm scale
- N10O remove cationic Sb but not metallic or anionic one
- in the case UO_2^{2+}, real samples from several mines
- good removal even if samples contained a huge excess of other metal ions, like Na^+, Ca^{2+}, Mg^{2+}, ...



	Removal efficiency [%]	
Company	Th	U
Mine T	66,1	96,1
Mine T*	99,9	100
Mine K	-	100
Factory X	-	99,1
Mine L	-	100

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N10O in 100 m^3 scale

- laboratory tests are made in 100 ml
- 10-100 l scale experiments with SoFi filtration instrument is in progress (Savonia)
- at the moment ca. 30 kg of **N10O** is available for tests
- during the next winter first tests in 1 m^3 scale and hopefully on spring 2014 in 100 m^3 scale

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Wet chemistry alliance

Synthetic chemistry

Prof. J. Vepsäläinen (UEF)

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Ph.D. J. Weisell (Academy, SEEWAY)
Ph.D. M. Häkkinen (UEF-Spear, TEKES)
Ph.D. J. Leppänen (UEF)
Ph.D. N. Jukarainen (Open)
M.Sc. A. Alanne (Academy, 2014)
Tech. M. Salminkoski (UEF)
M.Sc. K. Aho (Open, 2015)*

*not as active students

Biogenic polyamines

Prof. L. Alhonen (UEF)

Ph.D. T. Keinänen (UEF-Spear)
Ph.D. M. Hyvönen (Academy)
M.Sc. S. Ucal (Academy)
Tech. T. Reponen (UEF-Russian)

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M.Sc. S. Viitala(Company, 2014)
M.Sc. E. Sankala (UEF-Spear, 2014)
Student T. Pennanen (Company, 2013)
Student R. Mbi (2013)
Student L. Portin (2013)
M.Sc. T. Huhtala (Cerebricon, 2014)

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Student J-M Aalto (2014, SEEWAY)
Tech. H. Vepsäläinen (UEF)
Tech. K. Auvinen (Kuopio)

PhD students outside the alliance: M.Sc. J. Roi-vainen (2013), M.Sc. T. Soininen (2013)

Co-operation network

Campus Area

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Savonia AMK (E. Antikainen)
Labtium (L. Hämäläinen)
Prof. Vesa-Pekka Lehto
PhD Arja Tervahauta
Ph.D. doc. Jarkko Akkanen
SIB-lab (M. Selenius)

Co-operation with companies

MinTec (R. Neitola)
Talvivaara maining company (Jokiniemi)
EkoKem Oy (J. Osterbacka)
Sofi-Filtration (S. Aho)
Chemec Oy (L. Moilanen)
Mondo-Minerals
Dragon Maining
Agnico-Eagle Finland Oy
Aquaminerals Finland Oy
Kemira Oyj (R. Aksela)
....

National co-operation

Ph.D. J. Rämö (Oulu)
Prof. M. Haukka (Jky)
Adj. prof. E. Sievänen (Jky)
Adj. prof. M. Lahtinen
PhD R. Harjula (Hki)
PhD H. Hyvönen (Hki)

International co-operation

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Prof. M. Lecouvey (France)
Prof. A. Khomutov (Russia)
PhD D. Yunvarev (Russia)
Zschimmer & Schwarz Mohsdorf