Arsenic removal from mine waters with sorption

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Background 1

- Results presented are part of a TEKES-funded joint research project: ARSENAL – Arsenic Control in Mining Processes and Extractive Industry aiming at developing e.g.:
  - New mineral processing and **water treatment solutions** for arsenic removal
  - Novel bio-based treatment processes for arsenic containing wastes and streams
  - Monitoring and environmental risk assessment tools
- Research partners: GTK and TUT
- Industrial partners: Outotec, Kemira, Ekokem-Palvelu, Agnico Eagle Finland, Endomines, Nordic Mines, Pyhäsalmi Mine, YARA, Mondo Minerals
Background 2

- Arsenic is a world-wide challenge (drinking water, industrial waste waters)
- Arsenic is commonly associated with ores containing metals such as gold
- It is often leached in mineral processing
- Tightening environmental permits may create the need to treat mine effluents for removal of As
- Precipitation with Fe/Al salts is the “default” method for As removal from water
  - Proven technology
  - Requires chemicals, facilities and energy for mixing and clarification
  - Produces sludge to be disposed of
- Other methods include e.g membrane technologies, sorption, ion exchange and wetlands
Background 3

- Sorption is a physical and chemical process by which one substance becomes attached to another*
- Sorption could be a viable option for at least trace level As removal (before discharge to a river, lake etc.)
  - Could be operated as semi-passive processes (e.g. reactive barrier, filter-type solution)
  - No chemicals and less process control needed in comparison with precipitation-clarification techniques
  - Disposal/regeneration of spent sorption material
- Huge water volumes call for cost-effective sorption materials
- One of the focal points of present research was to find industrial by-product materials capable of removing arsenic efficiently from mine waters

* Wikipedia
As-removal from mine waters

- Focus on sorption techniques for removal of trace As-concentrations from water (final polishing step)
- Cost effective sorption materials (industrial by-products) and comparison to a commercial material
  - Granulated steel slag
  - Cast iron chips
  - Ash pellet
  - Waste rock
  - Glass beads (inert reference material)
  - Granulated ferric oxo-hydroxide (Kemira CFH12)
- Material pre-treatment for better comparability of results
- Comparison to precipitation tests
Lab scale experimental work on As removal

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| Characterization of sorption materials    | • Environmental properties (preliminary)  
• Surface area (BET)                                                                                                                                  | Leaching from sorption materials, technical suitability of materials                           |
| Characterization of waters (mine waters from Finnish gold mine) | • Concentration of elements and salts  
• Arsenic speciation                                                                                                                                  | Basis for planning of experiments                                                             |
| Assessment of maximum removal capacity    | • Batch tests with varying solid to liquid ratios, pH-adjustment                                                                                                                                     | Removal capacity, scaling of kinetic experiments                                              |
| Assessment of removal kinetics            | • Batch tests with varying contact times (most promising materials)                                                                                                                                    | Removal efficiency, scaling of kinetic experiments                                             |
| Kinetic experiments                       | • Up-flow percolation tests (most promising materials)                                                                                                                                               | Material behaviour in close-to-real conditions                                                 |
| Precipitation tests                       | • Batch tests with ferric salts                                                                                                                                                                       | Comparison to sorption tests                                                                   |
Batch sorption tests for As removal

- Batch tests with 24 h contact time, ion exchanged water spiked with As mixed with sorption material at varying solid to liquid ratios
- Initial As concentration 40 mg/l (As$^{5+}$)
- Analysis of As from water before and after test
- As-standard solution dominated the pH at lower solid to liquid ratios and material-pH at higher solid to liquid ratios
  - pH-fixed tests to evaluate the effect of pH
- As a result the maximum As-removal capacity of the materials (mg As / g material)
Maximum As-removal capacities from batch tests

Maximum As-removal capacity, mg As/g material

- Waste rock: 0.02
- Granulated steel slag: 2.3
- Ash pellet: 7.9
- Granulated ferric oxo-hydroxide (CFH 12): 14
- Cast iron chips: 46

Studies continued with these materials
Assessment of As removal kinetics

- Batch tests with varying material to water ratios
- Mine water from a Finnish gold mine, As-concentration 1.5 mg/l (initial 0.8 mg/l, spiked with As\(^{5+}\)), SO\(_4^{2-}\) 5 000 mg/l, pH 8.1
- Intermediate samples taken during tests to assess kinetics
Column tests for As-removal

- Mine water with As concentration of 2 mg/l fed to two columns (initial 0.8 mg/l, spiked with As$^{5+}$)
- Artificial water spiked with As$^{5+}$ (2 mg/l) fed to two columns
- Tests started with retention time (effective) of 60 minutes -> 30 min. -> 15 min.
- As-concentrations determined two times per week, wider analytics once/month
- Started in March 2013
Column tests for As removal

As concentrations, mg/l

As IN mine water
As IN artificial water
As OUT CFH12, mine water
As OUT CFH12, art. water
As OUT cast iron chip, mine water
As OUT cast iron chip, art. water

Time, days

HRT 60 min
HRT 30 min
HRT 15 min

As, mg/l

0,0
0,5
1,0
1,5
2,0
2,5
3,0
3,5
4,0
4,5
5,0

0 20 40 60 80 100 120 140 160
Precipitation tests for As-removal

- Mine water with As$^{5+}$ -conc. 2 mg/l (same water than in the column tests)
- Ferric sulphate (Kemira PIX-105) used as coagulant with varying Fe/As –ratios
- Batch tests with 30 minutes of mixing followed by filtration
- Intermediate samples were taken during tests to assess kinetics
- Data used in comparisons with sorption based As-removal
Scaling up the preliminary results – rough estimates

- Mine water with 2 mg/l As concentration, 1 million m³ per year: Annual As load of 2 000 kg

**Sorption based As-removal:**
- Approximately 5 mg As removed per 1 gram of garnulated ferric oxohydroxide (CFH12) so far
- 400 tons of CFH12 needed annually (and waste to be disposed of)

**Precipitation with ferric sulfate:**
- In this case 20 times molar amount of Fe³⁺ needed to reduce As level below 0,5 mg/l
- Approximately 30 tons of Fe³⁺ needed (10 m-% Fe³⁺ in chemical PIX-105)
- 300 tons of liquid ferric sulfate needed annually
- 123 tons of sludge created
Conclusions

- Industrial by-product material (cast iron chips) showed promising As-removal potential in batch tests.
- Technical problems faced in column testing (reactions with mine water caused clogging, under investigation).
- Commercial sorption material Kemira CFH12 shows good behaviour in column tests.
- Rough calculations show relatively big material consumption and chemical consumption for sorption based and precipitation treatment, respectively.
VTT creates business from technology