Nanostructured vermiculite -
A new material for recycling ammonium
from different types of polluted matters

The vermiculite research group at
University of Turku¹, Novia University for applied sciences² and Swedish Agricultural University³

Olav Eklund¹, Taina Laiho¹, Alexey D. Shebanov¹, Vesa Toropainen¹, Sten Engblom², Nina Åkerback², Kirsi Lahtinen¹, Kenneth Sahlen³ Miradije Rama¹ Juuso Suominen¹

Market potential by
Stefan Sandbacka, Luna CleanTech
Olli Mankonen, Turku Science Park
Timo Forss, NanoGeo Finland
Vladimir Rudashevsky, PC+ Ltd
Nadezha Matveeva, Rusnano Ltd

Business development laboratory, Turku School of Economics
Aim of this talk

- Present vermiculite and the new nanostructured product, **GT-1**, for use in ecologically sound and efficient removal of ammonium from polluted areas and its re-use as secondary product **GT-2** - soil improver for nitrogen depleted areas

- **Vermiculite is a waste product in carbonatite mines**

- Present the nanotechnology behind the invention
Raw-material for nanomodification

We use Kovdor vermiculite, Russia (Reserves - 22.9 mln tons)

\[(\text{Mg,Fe,Al})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH})_2\cdot4\text{H}_2\text{O}\]

Other methods of characterization used: XRD, AFM, TG, XPS and PIGE (MGC-20)
From vermiculite to GT-1 by nanomodification

Topographic AFM image of freshly cleaved vermiculite surface and a line profile from the image.

Water and some ions leave structure as a result of controlled heating – material gets adjusted by patent heating regimes (Patent FI 20050700)
GT-1

Lattice structure of GT-1 as the result of nanomodification of vermiculite

GS-1 material step height is diminished from 16 to 11.7 Ångström (Å)

Topographic AFM image of freshly cleaved GT-1 surface and a line profile from the image

[Image of AFM image and line profile]

<table>
<thead>
<tr>
<th>Line</th>
<th>Height [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Å]</td>
<td>0: 11.7 Å</td>
</tr>
</tbody>
</table>
Functional characteristics of GT-1

- Nanostructured geomaterial, filter and immobilizer of ammonium ion from different pollutions (water, soil, gas etc)
- Particle size – 3-5 mm
- Parameter $C_{d002} = 0.99–10.5$ nm
- Absorption capacity – 2.5-3.9 wt.% (up to 4.7 wt%)
- Speed of ion exchange – 20–60 min.
- Exothermic reaction
- Recommended pH <8
How does the invention work?
From GT-1 to GT-2

- Selective ammonium absorption tested in:
  - human urine
  - waste water from biogas plants
  - ammonium solutions
  - solutions with competing cations (K, Na, Ni, Cr)
  - combustion experiments (fox excrements)
  - industrial chimneys

The ammonium molecule is locked into the crystal lattice, and stays there!
Market opportunities

• **GT-1** has a business potential in:
  
  • dry toilet market
  • agriculture
  • waste water treatment
  • landfill
  • composting processes
  • slaughterhouses

Other areas with elevated \( \text{NH}_4^+ \)
Dry toilet market

\[ \text{NH}_4^+ = 800 - 1600 \text{ mg/l} \]

- Business starts in the Nordic countries
  (in Finland 500 000 summer cottages, dry toilets for festivals etc)
- Extensive market in the developing countries (270.000.000 people lack toilets in India)
- Red cross, WHO for sanitary education
Agriculture

$\text{NH}_4^+ = 80 \text{ – } 2700 \text{ mg/l}$

- Reduce the smell in farms (alternative solutions are not user-friendly and/or cost-efficient)
- Recover ammonia
- Protect water fronts from contaminated streams
- Ammonium doped material can be reused as soil conditioner
Waste water treatment

$\text{NH}_4^+ = 150-1700 \text{ mg/l}$

- EU-directive – reduce ammonia by 70%
  (for 80% of European population)

- Process development

- Most cost efficient in smaller water treatment plants
Landfill

$\text{NH}_4^+ = 100 - 300 \text{ mg/l}$

- Cold water streams with low ammonium contents
- 1100 landfill sites only in Finland
Composting

\[ \text{NH}_4^+ = 500 - 5000 \text{ mg/l} \]

- **GT-1** in composting processes increases the nitrogen content in the final compost.
Slaughterhouse waste destruction

\[ \text{NH}_4^+ = 300 - 800 \text{ mg/l} \]

- High nitrogen content in slaughterhouse waste
- Urban (European) problem
- Increasing problem with welfare
When **GT-1** has settled its mission as a selective ammonium absorbent, it starts a new life as **GT-2**, an improver for N-depleted soils.

Greenhouse experiments with GeoTrap-2 as soil improver. Seedlings growing in GT-2 (ammonium doped **GT-1**) are 10 times stronger than the reference seedlings!
Functional characteristics of GeoTrap-2

- **Ammonium-doped modified geomaterial**, fertilizer for a long period of use and soil conditioner
- Parameter $C_{d002} = 1.124\text{–}1.248 \text{ nm}$
- N – 2.5-3.9 wt. %; K – 2-3 wt. %;
  Mg – not less than 7 wt. %; H$_2$O – not less than 14 wt. %
- **Complex fertilizer – 2-3 seasons of use**
- Soil conditioner – several years of use
- **Ecologically friendly – not over-fertilizing the soil**
- Useful components being extracted by “silicate bacteria” gradually to the plant root zones, in various cases can be used as natural fertilizer for organic food
- **Water-insoluble – does not require special storage conditions**
Engineering solutions for GeoTrap-1 to GeoTrap-2 - process

Technical solution for purification of still waters (lakes, sediment basins)
AGRICULTURE

CHEESE!
Tests with manure sludge

GT-1 was mixed directly into the manure sludge: sludge + GT-1 (200 g + 20 g)

Time of experiment 48 h.

Starting material: Manure sludge
Dry matter of the sludge = 13.1 %

<table>
<thead>
<tr>
<th></th>
<th>Manure sludge (g/kg)</th>
<th>Dry matter (g/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total nitrogen</td>
<td>4.84</td>
<td>36.95</td>
</tr>
<tr>
<td>Nitrogen in solution</td>
<td>1.24</td>
<td>9.47</td>
</tr>
</tbody>
</table>

10% GT-1 in the manure sludge reduces 70% of its nitrogen.

The nitrogen content in GT-2 is 3.5 wt %
Reducing environmental loading from a feedlot
TEST: Reducing nitrogen from feedlot water

Water was collected from a feedlot.

400 ml of water from feedlot was mixed with 40 g of GeoTrap

Samples (30 ml of water and 2 g of GeoTrap-1) were taken for analysis.

Analysis were performed by FIA method at NOVIA Vaasa.
RESULTS FROM THE FEEDLOT TEST

Initial amount of ammonium ions is 8 mg/l
Ongoing research

The innovation works, we are now testing the technology in different case studies

- Biogas plants (ongoing pilot research)
- Water treatment plants (from case to case)
- Filters for chimneys (ongoing project, good results)
- Eko farming (ongoing projects)
- Recycling of GS-2 back to GS-1 (ongoing project)
- A company has been started, NanoGeo Finland, that will start to manufacture Geotrap
CONTACT

Prof. Olav Eklund
University of Turku
Department of Geology
Fi-20014
Turku, Finland
E-mail: olav.eklund@utu.fi
Phone: +358-44-2956429