Leading Global Producer of Halloysite Clay

Dragonite™ for Controlled Release of Active Agents

Andre Zeitoun
Ian Wilson, PhD
Yuri Lvov, PhD
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Who is Applied Minerals?

- Owner and operator of **Dragon Mine** in Utah, the only known commercial scale deposit of **Halloysite clay** in Western Hemisphere and one of only two in the world.

- The Dragon Mine contains a Halloysite resource of 596,700 tons of measured and 776,500 tons indicated.

- Resource evaluation was prepared independently by Dr. Ian Wilson, former Chief Geologist of English China Clays and then Imerys. World renowned expert in Halloysite clay as well as Kaolin, GCC and other Special Clays. Considered a “competent person” under JORC mining code, qualified to issue bankable feasibility studies.

- The company markets their product under the **Dragonite™** brand.
What is Dragonite™ Halloysite Clay?

○ **FORMATION:**
Halloysite is formed naturally through the hydrothermal alteration of various types of rocks over the course of hundreds of millions of years. Conditions for its formation are uncommon and the resulting deposits easily eroded if unprotected during formation. As a result, commercially viable deposits are extremely rare.

○ **PROPERTIES:**
Dragonite™ Halloysite Clay typically has a diameter smaller than 100 nanometers with lengths ranging from about 500 nanometers to 1-2 microns.

Traditional uses include fine china, advanced technical ceramics, fillers in paints and paper, food extenders, catalysts and molecular sieves.
30,000+ tons combined capacity through plant at Dragon Mine and outsourcing partner KaMin LLC, a leading kaolin producer

Material is immediately deployable in bulk via truck or nearby rail transportation
Louisiana Tech University - Institute for Micromanufacturing
• Integrated multidisciplinary research and technology commercialization with specialty in micro/nano scale technologies and systems
• 65,000 sq. ft. of R&D and user facilities

Transmit Technology Group
• Polymer research & development, testing, technical marketing
• Full lab and services available: Mixing, molding, processing, test specimen and testing
Morphology of Kaolin and Halloysite

1. PLATY KAOLIN
2. STACKS OF KAOLINITIE
3. TUBULAR HALLOYSITE
Dragonite™ Crude Ore
Characterization of Halloysite

1. XRD - Mineralogy
2. XRF - Major element chemistry
3. ICP-MS – range of trace elements
4. FTIR
5. Surface area
6. Porosity
7. Brightness and colour, ISO
8. Particle size distribution
9. SEM and TEM – morphology
10. Full range of product evaluation
XRD Scans of 100% Halloysite, Kaolinite and Mixture

DRAGON 26
100% HALLOYSITE
NO MODULATION

GSL BULK 5
99.2% KAOLINITE
MODULATION

DRAGON 22
64% HALLOYSITE
36% KAOLINITE
MODULATION
Carbon Nanotubes *versus* Dragonite™

**Parameters**
- Diameter / length
- Inner Lumen Diameter
- Biocompatibility

**Dragonite™**
- 50 / 1000 nm
- 15 nm
- Biocompatible

**Carbon Tubes**
- 2 / 1000 nm
- 1 nm
- Poisonous
Dragonite™ Halloysite Clay occurs in nature as hydrated mineral that has the formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\cdot2\text{H}_2\text{O}$ which is similar to kaolinite except for the presence of an additional water monolayer between the adjacent layers. It forms by kaolinite layer rolling due to the action of hydrothermal processes.
Potential Applications of Dragonite™

1) Paint with anti-fouling properties where marine biocide was loaded. Delivery of herbicides, insecticides, fungicides and anti-microbials
2) Release of anticorrosion agents in protective coating
3) Plastic fillers (strength, self-healing)
4) Drug sustained release (cosmetics), food additives, fragrance
5) Use in advanced ceramic materials, bio-implants
6) Specific adsorbent (oil, ions), hydrogen storage
7) Templating nanoparticle synthesis and molecular sieves
8) Catalytic materials (hydrocarbon cracking)
Dragonite™ Microscopy Images

SEM

TEM

AFM
Pore size distribution of Dragonite™ lumen obtained from N₂ adsorption measurements analyzed with BET model.

Zeta potential for Dragonite™ Halloysite Clay (middle curve), silica (blue), and alumina (red) nanoparticles.
Making Dragonite™ Tube Fluorescent With Aminopropyl Triethoxysilane-FITC

Trypan Blue test of Dragonite™ in HeLa (and MCF-7 tissue cells. % Cell Viability vs Dragonite™ concentration for 24-48-72 hours. It is much less toxic than usual table salt - NaCl (which kills cells at concentration of 5 µg/ml)
Release Profiles for Drug Loaded Into Dragonite™ in Water (10-hour release)

Brilliant Green

Mercury porosimetry of Dragonite™ Halloysite Clay unloaded and loaded with drugs
Low charged at neutral pH insulin (2 nm diameter, pKa 7.1), urease (6 nm, pKa 6.2), and positive at neutral pH peroxidase (diameter ca 3.5 nm, pKa 8) show faster release than negative catalase (9 nm diameter, pKa 5.5), glucose oxidase (7 nm, pKa 4.2), and acetylcholinesterase (diameter ca 8 nm, pKa 5.5). 5-10 hours versus 100-150 hours.
General Procedure for Preparation of Dragonite™ Halloysite Clay-Paint Composite for Corrosion Protection

1. Initial Halloysites
2. Inhibitor Loading
3. Washing
4. Incorporation into Coating
5. Polyelectrolyte Shell Assembly

Nanocontainers in Hybrid Coating
Protective chemicals (corrosion inhibitors, antifouling agents) slowly release from the Dragonite™ tubes when cracks occurred.
Benzotriazole Corrosion Inhibition Mechanism

Corrosion process is going on in the absence of corrosion inhibitor

Benzotriazole effectively stops copper from corrosion by forming protective layer on the surface of the metal

Structure of benzotriazole iron (II) and copper benzotriazole complex
Polyurethane paint after 6 month of exposure to 30g/L NaCl

Dragonite™-Paint composite, loaded with 8-hydroxyquinoline

Dragonite™-Paint composite, loaded with benzotriazole
Halloysite is readily mixed with a variety of metal protective coatings, which is an important advantage. Above-stress-strain characteristics of halloysite-paint composites with different halloysite concentration.
Dragonite™-Paint Composite Surface Properties

Water contact angles on Dragonite™-paint composite surfaces
Paint Adhesion Test on 2024 Al Plate

\[ F = \frac{(P + b)L}{\alpha}(\text{ctg}(\beta) - \mu) \]

\[ W = \int F \cdot dy \]

<table>
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<th>Halloysite concentration (%)</th>
<th>Maximum force (N)</th>
<th>Energy/area (kJ/cm²)</th>
<th>Paint remained (%)</th>
<th>Squares peeled off (%)</th>
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<th>Halloysite concentration (%)</th>
<th>Maximum force (N)</th>
<th>Energy/area (kJ/cm²)</th>
<th>Paint remained (%)</th>
<th>Squares peeled off (%)</th>
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<td>22.63 ± 5.74</td>
<td>0.21 ± 0.03</td>
<td>6</td>
<td>2 ± 1</td>
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Epoxy

Polyurethane
Paint Resistance to Rapid Deformation

Deformation energy (J) vs. Halloysite concentration (%)

- A366 Fe alloy
- 2024 Al alloy

Epoxy samples after impact without (left) and with (right) 3% Dragonite™ loading. The Dragonite™ prevented cracking of the epoxy material.
• Release rate may be controlled by geometry of Dragonite™ Halloysite Clay (tubes with smaller internal diameters provide longer release). We operate with smallest 15 nm diameter lumen.

• Rate can also be controlled through: formation of stoppers at tube endings, or with encapsulation of tubes by layer-by-layer (LbL) nanoassembly of polyelectrolytes (beginning with polycation complexation)
Benzotriazole Release from Halloysite in Water

(For Comparison - red curve dissolution of free non-encapsulated benzotriazole)
Corrosion Inhibition Kinetics and Long Time Protection Through Sustained Triazoles Release

Kinetics of BTA deposition on Cu surface studied by QCM. Process follows 1st order kinetics with the constants of 0.012 and 0.0033 for fresh and salty waters respectively.

Copper strips were painted with polyurethane paint from top side and acrylic latex paint from the back side and artificially scratched. Blank was painted with usual paint, others had Dragonite™ loaded with specified corrosion inhibitor and admixed with acrylic paint. Strips were exposed to water containing 30 g/L NaCl.
Two copper strips were painted with oil based blue paint (ECS-34 powder, blue, produced by Tru-Test manufacturing company) for corrosion resistance testing. Dragonite™ loaded with benzotriazole was mixed with paint before painting sample (A). Both of the strips were artificially scratched and exposed to highly corrosive media containing 24 g/l NaCl, 3.8 g/l CaCl2, and 2 g/L Na2SO4 for 10 days.

After exposure, corrosive media was analyzed for Cu (II) content. Copper in corrosive media were detected by UV-Vis spectrophotometer, and 120 ppm of copper ion was observed in the media where sample (B) was exposed while no copper was detected in the media of sample (A).

Copper strips were painted with polyurethane paint from top side and epoxy paint from the back side and artificially scratched. Strip at (a) painted with usual paint while strip at (b) had Dragonite™ loaded with benzotriazole admixed with epoxy paint. Strips were exposed to water containing 30 g/L NaCl.
Formation of Coating / Stoppers Through Dragonite™
Rinsing in Aqueous Copper Ions

While suspending in Cu(II) solution benzo triazole starts leaking from halloysite nanotubes.

Leaking benzo triazole molecules meet with Cu(II) ions at tube endings.

Copper-Benzo triazole film is formed at tube endings from interaction between Cu(II) and benzo triazole.
TEM With Elemental Analysis; Dragonite™ Coated with Cu-Benzotriazole Complex Layer

- Nitrogen mapping
- Overlap mapping image (Nitrogen and Oxygen)
- Oxygen mapping
Dragonite™ Tubes As Containers for Anticorrosion Coating With Benzotriazole (Stoppers)

Benzotriazole release with different stoppers at the tube ends

CCD images (top) and current density maps (bottom) of Al coated with sol-gel layer immersed in 0.1 NaCl after 0, 4.5 and 10 h; left - without Dragonite™, and right - doped with benzotriazole loaded Dragonite™
Encapsulation of Dragonite™ With LbL Assembly of Polyelectrolytes (e.g. Chitosan Complexation)

Alteration of surface charge during LbL assembly as well as deposition of 7 nm SiO₂ nanoparticles on Dragonite™ surface clearly indicates that the assembly was performed successfully. An average thickness of PEI/PAA bilayer is 2.2 nm. PEI - poly(ethyleneimine), PAA - poly(acrylic acid)
Epoxy Self-Healing with Hardener Loaded Dragonite™

SEM of fracture surfaces of 10 wt% Dragonite™-epoxy composite: (a) debonding and breakage of Dragonite™ and (b) pull-out of Dragonite™

Stress-strain relationships of Dragonite™/epoxy composites prepared by adding Dragonite™ as a dry powder. Sample dimensions 17 x 8 x 0.6 mm and pulled with the speed of 0.6 mm/min.

Antifouling, Antimolding Pain Doping With IPBC (Iodobutylpropyl Carbonate) Loaded Dragonite™

(a) Paint with inclusion of Dragonite™ containing an antifouling agent. (b) Mold growth inhibition: number of colonies vs days (blue, untreated; purple, treated growth media).

**Figure 4.** Slow release of IPBC from halloysite and kaolin.
Nanotemplates for Synthesis and Storage of Materials

Synthesis without loading

C and Cu signal arises from the TEM grid.
Conclusions

1. The capability of naturally occurring Dragonite™ Halloysite Clay as a container for protective agents (corrosion inhibitors, antifouling) was demonstrated. Inhibitors may be kept in such containers for a long time and released in the coating defect points within tens hours. Efficiency of paint doped with triazoles-Dragonite™ was demonstrated for copper, aluminum and iron protection.

2. Once loaded with protective agents, Dragonite™ Halloysite Clay can be modified by formation of stoppers at tube endings to extend release rates to hundreds hours.

3. Dragonite™ is mixable with variety of polymers and paints. Physical properties of Dragonite™ / paint composites were improved (strength).

4. 3-5% Dragonite™-polymer composites increase tensile strength for 30-50%; self-healing of the composites micro-cracks were demonstrated.

5. Synthesis of silver nanorodes in Dragonite™ lumen was performed.
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References


