Chemical Considerations in the Thermal Desorption Remediation of Soils.

CLRA/ACRSD: *Reclamation - A Changing Landscape*.

SMART Remediation Seminar 2013

Darryl R. Nelson & Nick Platts.

Nelson Environmental Remediation Ltd., Spruce Grove, Alberta.

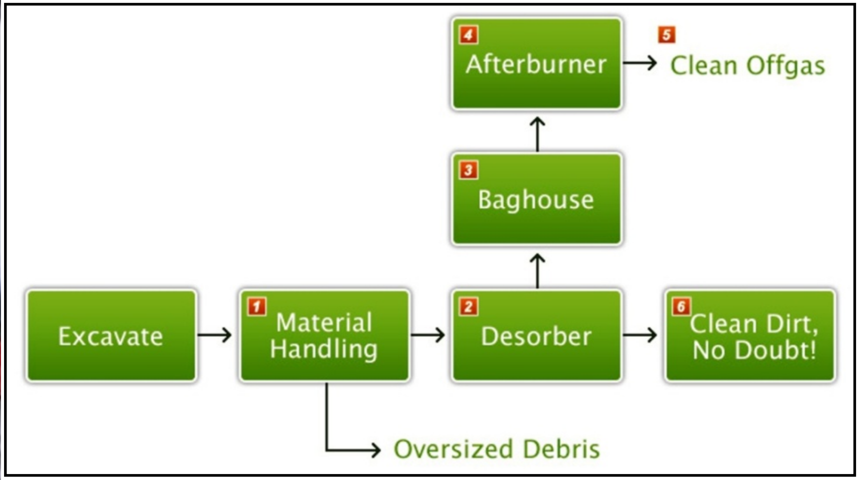
Clean Dirt, No Doubt!

www.nerglobal.com

Benefits of Working with NER's TDU Systems:

- Predictable time-frame;
- Mobile, on-site equipment;
- Measured quantity;
- Competitive pricing;
- Re-use quality of treated soil;
- Liability management.

TDU Operational Process Overview:



TDU Site Overview:

Projects…

NER’s fully-mobile TDU plants:

- ***ex-situ*** **thermal desorption cleans soils impacted by PHCs** (incl. crude oil, diesel, jet fuel, *etc.*), as well as a wide variety of **commercial organic chemicals** (incl. solvents, pesticides, chlorocarbons, *etc.*);
- applicable to small-molecules (final-products, congeners, side-products) & some higher molecular-weight species (e.g., PAHs, phenols, “*asphaltenes*”);
- a mobile TDU plant can reach practically any location (*e.g.,* by barge/ship out of Seattle, WA, or Houston, TX).

Applicability considerations:

Organics:

- HCs F1-F4 (BTEX, C_6-C_{10}, C_{10}-C_{16}, C_{16}-C_{34}, C_{34}-C_{50});
- polynuclear aromatic compounds, PNAs (incl. PAHs, PANHs, PASHs);
- oxygenates (glycols, dioxanes, alcohols, phenols, aldehydes, ketones, carboxylic acids, esters, ethers);
- chlorocarbons (chlorinated solvents (CH_2Cl_2, *etc.*), TCE, PCE, HCHs ("BHCs"), BHC, PCBs, PCDDs, PCDFs);
- Sulfur-containing spp.; Nitrogenates / amines / 4° ammonium ions; Phosphorus-containing spp.
- herbicides (*e.g.,* Tebuthiuron, Bromacil).

Inorganics:

- metals (electrochemical series, reducibility, volatility, toxicity);
- ions (*e.g.,* phosphate, sulfate, *etc.*, *vs.* ammonium, nitrate, sulfide, chloride, fluoride).

Physical parameters of soil:

- pH (both native/ambient, & as a site-specific function of T, esp. re: HCl, HF, *etc.*);
- calorific values (calc. from VOC analyticals, *vs.* total by bomb calorimetry);
- mineralogy (clay minerals, salinity, sedimentary rock);
- moisture content (% H_2O);
- temperature;
- redox condition (reducing, oxidizing).

Dirt prep. aspects & emissions controls:

- ground disturbance / excavation, screening, crushing, homogenization, sloping, *etc.*;
- wind-rowing / turning-over for pre-drying (re: H_2O's high C_p);
- stoicheiometric admixture of *p*H amendment/s (*e*.*g*., $CaCO_3$ / $Ca(OH)_2$; $CaSO_4 \cdot 2H_2O$ / elemental Sulfur);
- stoicheiometric admixture of precipitants (*e*.*g*., hydroxy-apatites for Pb(II));
- continual optimization of the redox conditions in the thermal oxidizer unit;
- alkaline wet-scrubbing for small-molecule inorganic acid volatiles & acidic gases (*e*.*g*., HCl, SO_2).

NER's TDU process for soil remediation:

- "mobe", site prep., dig up the "*dirty dirt*", chase-the-plume;
- "*soil prep*." as required (*e*.*g*., screening, crushing, pre-drying, *p*H amend);
- break up the dirty dirt & feed it into the TDU (small lumps);
- tumble / heat / low-O_2 inside the TDU to desorb HCs/VOCs;
- promptly re-hydrate the "*clean dirt*", typically about 200 litres/T to wet-down dusts & reach 8-12 % moisture content for proper soil compaction during backfilling (the optimal % H_2O depending on the soil type);
- oxidize the HCs/VOCs as efficiently as possible through to CO_2 & H_2O;
- samples of the processed soil sent for laboratory analysis (resp. AENV/CCME/USEPA/*etc.* criteria);
- backfilling of post-confirmatory clean soil;
- contour / landscape / seed / re-plant, per the landowner's direction;
- "demobe" & an 'after-party' for the hard-working crews.

So, after the formal soil treatment itself, what of the below-Tier residual organics left behind?

Has bearings on questions such as:

- Tiered concentration limits in the future?
- TDU-induced chemical transformations?
- Effects on site ecology?
- Other 'sustainability' issues?

Hot (~500 °C or ~900 °F).

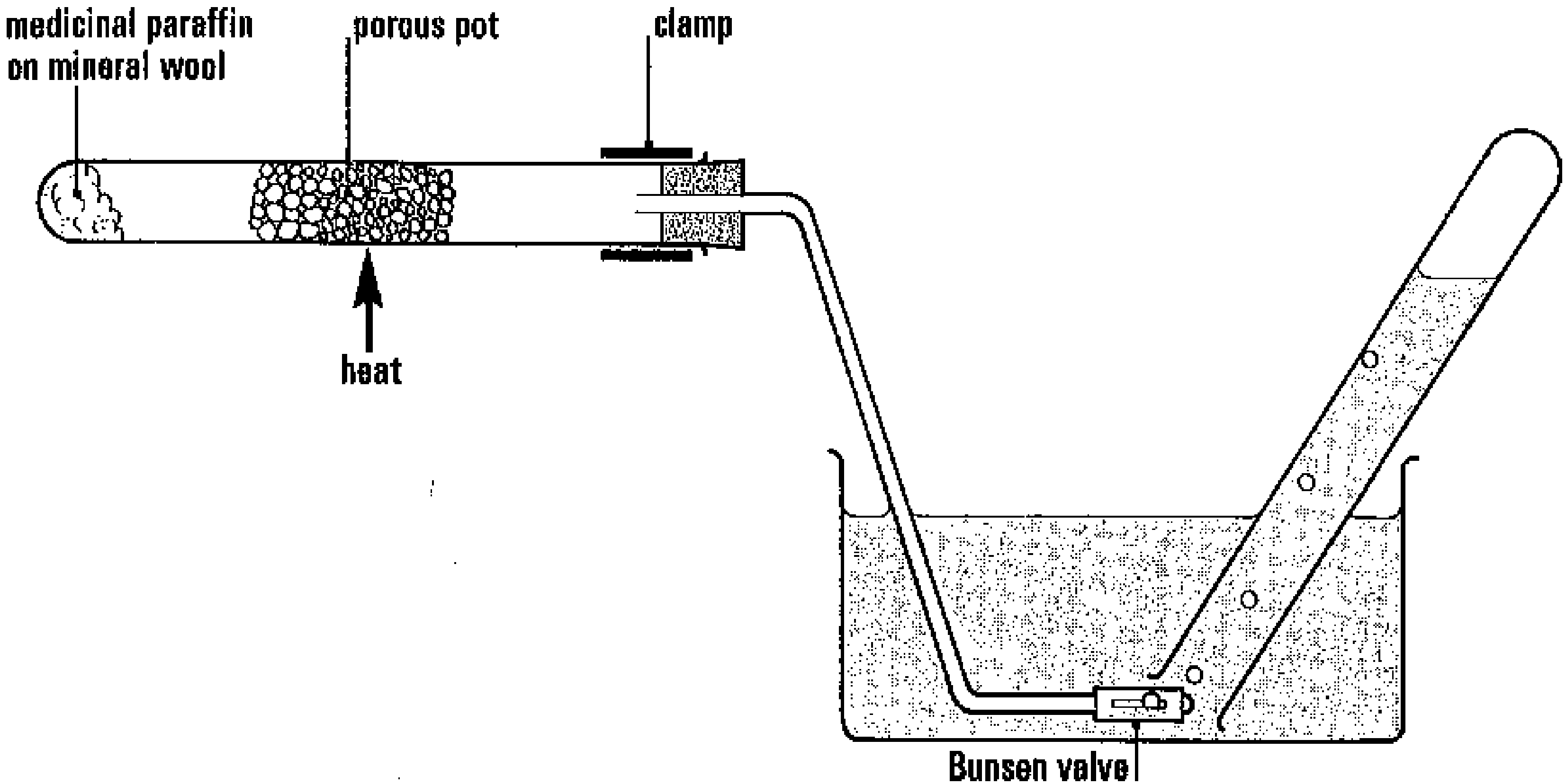
Dry (*cf.*, water's high dielectric constant).

Anoxic (i.e., extremely low O_2).

Freshly-exposed mineral grain surfaces (i.e., both mechanically & thermally).

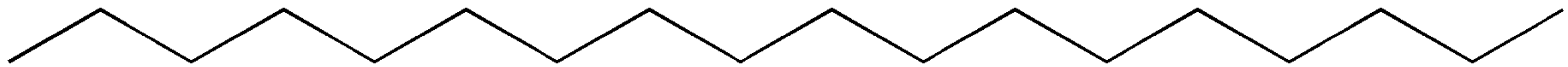
Clay minerals (common soil phyllosilicates; very high surface areas per gram).

Chemically-reasonable expectation of essentially **uncontrolled heterogeneous catalytic cracking reactions** (*cf.*, 1940s).



Classic catalytic cracking experiment.

PHC F3 ($>C_{16}$ - C_{34} range), e.g., n-Octadecane, $C_{18}H_{38}$



Clay mineral (hot-dry-anoxic-activated inorganic surface).

e.g., n-Octadecane ($C_{18}H_{38}$)

Hot, dry, anoxic,
& freshly-exposed
clay mineral surfaces.

⇓

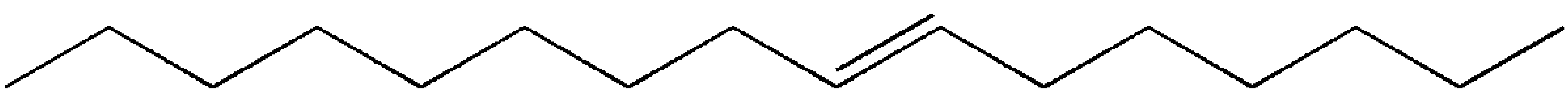
Inorganic heterogeneous
cracking catalysis.

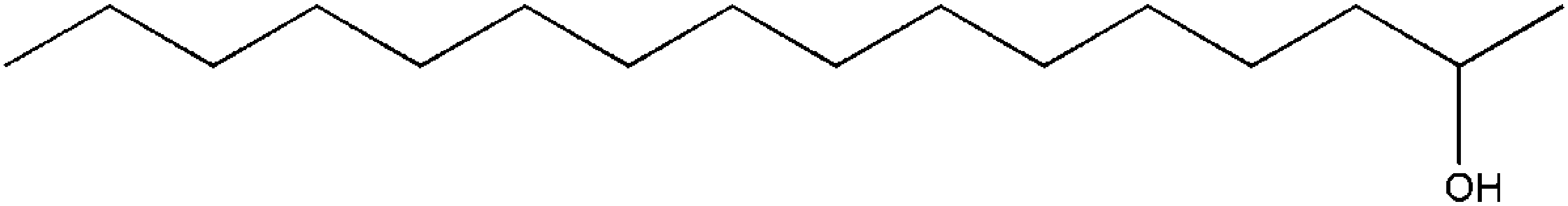
n-Hexadecane ($C_{16}H_{34}$) + ethene (C_2H_4).

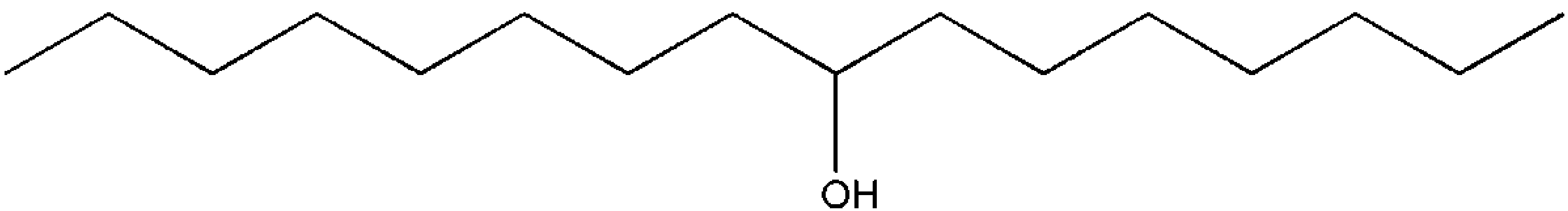
Classical/Textbook experiment…

…*versus* chemical reality:

alkane/paraffin “smash & bash” Chemistry (*e*.*g*., thermal & catalytic cracking) typically produces a wide variety of chemical side-products & a variable product distribution.







Chemical reaction types expected:

Thermal & catalytic cracking rxns (essentially uncontrolled);
Hydrolytic addition rxns (during aqueous quenching);
Aerial oxidation rxns (in the "clean dirt" pile);
Mechanochemical rxns (at freshly-exposed inorganic surfaces).

Chemical expectation of a **wide product distribution** of functionalized residuals, including: chain branchings, alkenyl functions (*t* & *i*), various oxy-functions (incl. hydroxy, oxy/ketone, carboxylic acid).

Ecological Implications:

Organic functionalities process-introduced into residual PHC skeleta provide **molecular '*handles*'** (*i.e.,* in the Fischer '*lock and key*' analogy/model) that enable microbial enzymatic action (assists / encourages / accelerates bioremediation among the complement of residuals).

A beneficent & value-adding 'gift' for the client at demobilization.

What of Other Soil Remediation Methods?

If the PHC-remedial method **has hot-dry-anoxic conditions & a class of catalytically-active inorganic(s) that are either entrained/exposed**, your suite of residual organic compounds will contain site-new chemical spp. (via thermal / catalytic cracking, (de)hydrogenation, hydrolytic addition, partial oxidation, (de)carbonation, *etc.*) with molecular '*handles*' for microbial activity.

But if the PHC-remedial method is **wetted** all the way through, mineral surface catalytic activities will generally be **quenched** (*i.e.*, heterogeneous catalytic activities will be inhibited).

Beneficences at TDU "demobe":

- below-criteria soils (re: PHCs, VOCs);

- maintain the original site-complement & proportions of inorganic mineral phases & ion availabilities (resp. microbial growth surfaces, mineral ion providences, ion exchangeabilities, native *p*H-buffering capacity, *etc.*);

- functionalized/derivatized PHC/VOC residuals that are metabolically available (esp. in the case of the various oxy-function molecular '*handles*' that are possible).

The landowner’s perspective:

- can take credit for ecologically responsible behaviour (*cf*. hauling off to landfill & then importing site-exotic backfill);

- is pleased to know that below-criteria residuals will be further remediated on microbial recolonization of the soil (metabolic & enzymatic processes operating on TDU-induced molecular ‘handles’ / functionalities).

Mechanochemistry / Tribochemistry.

- Tribology (Gk., *tribo* “to rub”) is a field most commonly come across in lubricants technology (industrial applications, R&D).
- Tribochemical changes are wrought on molecules (*e*.*g*., lubricant oils) in mechanical settings, owing to factors such as: high T; T-cycling; frictional forces; reactions with O_2/H_2O, metals/alloys, oxides/sulfides (*e*.*g*., redox rxns, hydrolyses, (de)hydrogenations, (de)carbon(yl)ations, heterogeneous catalyses).

Mechanochemistry during soil remediation.

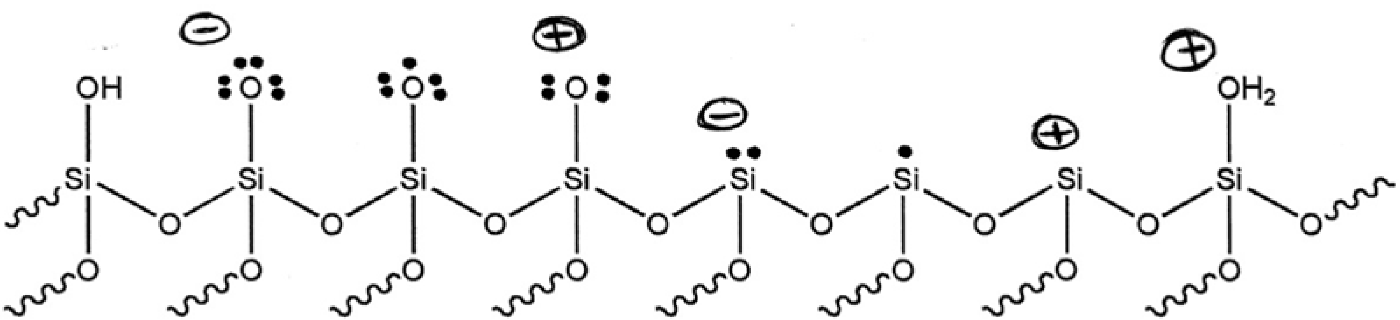
Inorganic surfaces (*e*.*g*., quartz) are energetically 'activated' (*i*.*e*., made much more chemically reactive than normal) during mechanical handling/operations due to frictional heating (*e*.*g*., Qz 'sparks'), electrification (frictional/static & piezoelectric), & by the sudden bond fissioning (heterolytic & homolytic) necessarily occurring at mineral grain/crystal fracture surfaces at rupture.

Covalent bond fissioning.

- *Heterolytic* bond fissioning generally results in full electrical (*i*.*e*., opposite ionic) charges on the two atoms being separated, typically producing a cationic moiety & an anionic moiety.
- *Homolytic* bond fissioning generally results in two (generally uncharged) free-radical moieties, each bearing an unpaired electron.
- Sudden bond-breaking can occur either mechanically or thermally (*e*.*g*., T quenching).

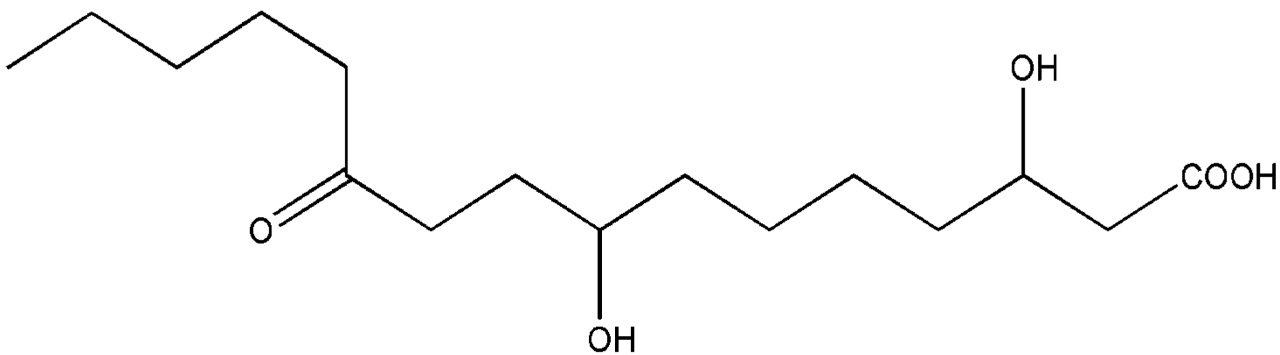
$O_{2\,(g)}$ $H_2O_{\,(g,\,l,\,c)}$

Exemplar PHC (F2/F3): *n*-hexadecane, *n*-$C_{16}H_{34\,(g,\,l,\,s)}$



Freshly-fractured mineral surface uppermost (*e.g.*, quartz, $SiO_{2\,(c)}$), bearing highly chemically reactive spp. (typically transient / short-lived), incl. oxidizing, reducing, free-radical, & acid/base spp.
The 'ideal' mineral inorganic crystal structure (*e.g.*, Qz '*giant molecular*') is understood to remain undamaged & essentially unaltered below the freshly-generated surface.

An exemplar of a mechanochemical final-product: *n*-hexadecan-3,8-dihydroxy-11-oxo-1-oic acid.



The most likely f.p. oxy-functionalities introduced into mechanochemically-reacted PHC substrates (*i.e.*, via chemical reactions involving freshly-generated mineralogic silicate/silica fracture-surfaces) are hydroxy (ROH), keto (R(CO)R'), & carboxylic acid (RCOOH) functions. Such mechanochemically-derived product suites can thus be anticipated to contain a mixture of alcohols (both terminal & internal), ketones, carboxylic acids, & multifunctional spp. (*e.g*., hydroxy-acids, keto-acids), all of which offer molecular 'handles' for microbial enzymatic action (generally degradative). Other oxy-functions such as aldehyde, ether, ester, peroxy, epoxy, etc., are possible, as are products of chain cracking (esp. free-radical induced).

Thank you for your attention.

Darryl R. Nelson, *President & CEO.* dn@nerglobal.com

John T. Tucker, ERM, B.A. Geog., *Technical Business Director.* john@nerglobal.com

Garry K. Ogletree, *Director, Business Development.* garry@nerglobal.com

Nick Platts, Ph.D., P.Chem. nick@nerglobal.com

Nelson Environmental Remediation (NER) Ltd.

www.nerglobal.com

(780) 960-3660.