Low Temp Thermal Treatment of Special Organic Wastes in Soil

Paper 26

Presented at the
33rd International Conference on Thermal Treatment Technologies & Hazardous Waste Combustors
October 13-15, 2014
Baltimore, MD

Thomas F. McGowan, [1] PE; [1]TMTS Associates, Inc, Atlanta, GA

Abstract

Direct and indirect fired low temp thermal desorption has been used in the US and worldwide since the 1980's to treat organic contaminated media.

This paper focuses on the problem areas in the technology and limits of the technology as applied to more difficult-to-treat organics -- such as PCBs, dioxins and explosive contaminated soils -- and to newer markets such as diesel based drilling mud. Media issues are also covered, from easy to handle sand to more difficult clays and silts.

Based on the authors more than 25 years of work in this sector working for OEMs, thermal service contractors and major engineering firms, the paper covers waste testing and matching the feed to the equipment, feed preparation and feed moisture content, the basics of solids handling, achievable and appropriate stack limits and required air pollution control equipment.

The key to a successful project is good soil testing for combustion-based properties, then matching the layout (e.g., cocurrent vs. countercurrent flow) of the system, establishing the right product and oxidizer temperatures, and selecting intermediate (e.g., hot cyclone) and final (e.g., baghouse, acid gas absorber) air pollution control elements.

Case studies on full scale projects are included, both in the US and worldwide.

INTRODUCTION

This paper covers material that is well known to experienced hands in the field, but is frequently missed by new service contractors, as well as regulators, that are not as familiar with the technology and its limitations. Primary issues having to do with setting project goals and associated system design are covered first, followed by national and international project case studies where thermal treatment plants succeeded in passing required quality objectives.

The major issues are covered in the following order:

- Site characterization/soil testing and setting clean up objectives
- Choosing appropriate thermal treatment and APC (air pollution control) equipment
- Feed preparation and material handling
- Passing stack tests and product quality guarantees

SITE CHARACTERIZATION/SOIL TESTING/ SETTING CLEAN UP OBJECTIVES

There are two levels of tests that should be considered when designing a site-remediation project:

- Standard lab tests that use small samples (typically 1 gram) and
- Larger-scale treatability tests, which are usually carried out in a muffle furnace (a small, high-temperature laboratory oven), bench top equipment or pilot units. With these tests, time and temperature can be varied to assess how clean the soil gets for a given set of operating parameters.

The standard tests that are described below are relatively inexpensive to conduct, fast to run and yield reliable results. Results can be used quantitatively. For example, the heating value can be used to judge the amount of auxiliary fuel required to treat the soil, or the amount of feedstock dilution with cleaner soil required if organic concentrations are too high. Similarly, test results can be used to define the amount of drying agent required to reduce the moisture content below the plastic limit to make material handling easier.

The results of these tests can also be used to help the engineer make qualitative judgments, such as those related to selecting the appropriate material handling, thermal-desorption, and air pollution control equipment. Be aware that the tests described below are not the typical "US EPA SW-846 8000" series using solvent extraction plus GC (gas chromatograph) to assess organic hazardous constituents for regulatory purposes. Rather, the ASTM (American Society of Testing and Materials) tests are used to better match the treatment process to the waste at hand, and experience has shown that "EPA type" organic tests, such as extractive Method 8270 for semivolatile organics, routinely understate the amount of total organic constituents in a soil. Keep in mind that soils commonly contain cellulosic/woody material (leaves, roots, kerogens, peat). This woody material is about 80% volatile, and 20% fixed carbon, and much of the volatiles will be released via low temp desorption, adding to the fuel value going to the oxidizer or condenser.

When experienced personnel select the right standard laboratory tests and review the results, more extensive treatability testing are rarely required. Treatability tests are typically reserved for unusual soil matrices, the presence of out-of-the ordinary contaminants (such as polymers), or new or unproven types of thermal treatment systems. The may also be run by contractors that are not yet experienced with a particular type of waste and want to better quantify costs, reduce risk and boost their chance of success.

Table 1 shows major soil parameter's and associated issues, and Table 2 shows critical ASTM system design-related tests, and more detail and additional tests can be found in reference 1.

Table 1, General Soil Parameters and Design/Operation Issues

Parameter	Design/Operation Issues
Organic concentration	Critical for safety concerns and for capacity estimation
Organic boiling point	Critical for ability to produce clean soil and to prevent condensation in the baghouse on countercurrent systems; dictates solid product temperature
Soil matrix (e.g., sand, silt, clay, gravel) and particle size	Required for material handling, feed prep, and soil cooling and consolidation and air pollution control
Soil moisture content	Affects material handling as well as capacity and fuel cost
Chemical compounds	Existence of chlorine and sulfur may require a scrubber and chlorine can trigger dioxin testing; affects regulatory costs and scrubber reagent costs

CHOOSING APPROPRIATE THERMAL TREATMENT AND APC EQUIPMENT

The Atterberg limits and related civil/soils engineering tests are useful in determining soil properties for thermal treatment projects. The major issue is how sticky and cohesive the material is, indicating at least use of dual feed augers into the desorber drum, or a slinger belt for very sticky material. In short, any soil close to its optimum moisture content on a Proctor Density test will be cohesive, with clays and silts being the biggest headache for operating personnel. High fines content soil calls for use of a dual arm pugmill or rotary cooler to successfully wet and cool the product.

If sulfur and/or chlorine are over the regulatory limit without control, dry lime injection into a baghouse or use of a wet scrubber will be required.

If the waste contains significant fuel-bound nitrogen, and local air limits are strict, then NOx control may be required via SCR or SNCR.

TSCA (Toxic Substance Control Act) wastes such as PCBs will require higher oxidizer temperatures to achieve higher DRE levels, and this increases slagging concerns in the oxidizer, increases fuel use, reduces system capacity and raises NOx emissions. More time consuming and higher cost stack testing is required for TSCA wastes.

A high concentration of high boiling point organics suggests use of cocurrent direct fired desorbers to prevent condensation of organics in the baghouse and the potential for baghouse fires.

Table 2, ASTM Tests Critical for System Design

Test Method/Comments	**Effect on Design/Operation**
Higher Heating Value - ASTM D1989 via automatic calorimeter	LEL and safety issues; maximum capacity, fuel use in oxidizer
ASTM D5142 Proximate, for mc, vm, fc, ash, at 950ºC	Volatile material (vm) and ash can be used to infer upper limit of organic content
ASTM D3176 Ultimate Analysis modified, for C, H, N, Cl, S, O by difference, ash, mc	Carbon and hydrogen can be used to infer organic content in the absence of carbonates; S and Cl, if organic, have impact on scrubbing costs; if S and Cl are known to be in organic form, tests should be run to assess scrubber needs
Ash Fusion Temperature - ASTM D1857 (oxidizing and reducing)	Required for clays and silts with sodium and potassium with cocurrent desorbers where slag may form in the oxidizer
Moisture Content - Gravimetric@105 C (not required if D5142 is done)	Capacity, fuel cost, need for lime pretreatment
Screen Fractionation (particle size) - ASTM D410	Helps to define what type of air pollution control system is required.
Bulk Density - ASTM D292	If job is bid on in-place cubic yards, required for conversion to mass basis for costing

Indirect fired desorbers fed waste which originally contained oil/water emulsions (e.g., "API separator sludge" from refineries), can be expected to produce emulsions in their condensed liquids. Traditionally the emulsions require heating to about 180°F (82°C) (and perhaps use of deemulsifiers) to break the emulsion, followed by centrifuging if good quality oil is required as a final product.

Dioxins[2] do not exist above 800°C (1472°F), hence oxidizers are an effective way to destroy them if they exist in the feedstock. However, they can form downstream of desorbers and oxidizers in gases which contain Cl2 and HCl via "de novo synthesis" at lower temperatures, with peak formation occurring between 572-662°F (300-350°C) and the range of formation being 392-842°F (200-450°C). Temperature is not the only factor, as particulates containing carbon, chlorides of alkali and other elements can speed the reaction. Recent calculations suggest that air-to-air heat exchangers have a shorter residence time in the critical temperature dioxin formation range than do dry bottom quench towers. A slow quench, as might be found using a waste heat boiler, should be avoided. Keeping the baghouse temperature below 450°F (232°C), and more preferably below 400°F (204°C) is also a good idea to minimize dioxin formation.

FEED PREPARATION AND MATERIAL HANDLING

The norm in the field is to screen to 2" (5 cm) top size, and use a magnet to remove tramp steel prior to feeding soil to the desorber.

Moisture content must be within the limits of the feed system, and mud rings may form in desorbers with excessively high moisture content feedstocks. Higher moisture content results in lower system throughput and more fuel use. Back mixing feed with dry product or mixing feed with pelletized quick lime (CaO; note -- there are hazards associated with this material) can also fix the wet feed issue.

Most plant operators feed the system at a constant ton per hour rate, then adjust other system parameters to achieve operating and compliance goals. <u>It is critical that the "blend master" working the pile and feeding the system mix soils upstream to prevent swings in moisture and organic content.</u>

For energetic waste, there is a maximum concentration in a mineral matrix that should not be exceeded to prevent the material from becoming detonable. <u>The services of an explosives expert should be sought for such projects to ensure safety both in feed preparation and thermal processing.</u> Some sites also have UXO (unexploded ordnance), which must be found and removed prior to thermal processing.

PASSING STACK TESTS AND PRODUCT QUALITY GUARANTEES

Equipment vendors should not guarantee the impossible, nor should regulators set impossible project objectives. Examples include:

- Setting the organic content in the desorber product *below detection limits.* Rather, a *reasonable* value should be chosen well above the lab detection limits, and one that is sufficient to protect the environment without adding excessive cost.
- Setting APC goals (such as gross particulates) below levels achievable by normal industrial standards.
- Calling for very low limits of benzene in product soil (or stack). Benzene is a ubiquitous byproduct of combustion and desorption, and trace amounts are commonly produced by heating woody material in soil.
- Requiring high organic DREs when processing soils with low organic feed concentrations (spiking would be required to prove out DRE)
- Regulators requiring both higher stack oxygen and higher oxidizer outlet temperature than what was experienced during system testing; you can have one or the other, but not both!

CASE STUDIES

Brunei/Negara Brunei Darussalam

System Owner/Operator: Envirosoil LTD

System Type: ASTEC indirect fired rotary desorber, condenser, oxidizer, oil water separator,

Site and Issue: Treatment of oilfield wastes from oil exploration and production activities, predominantly containing aliphatic hydrocarbons, but also polyaromatic hydrocarbons, asphaltenes, hydrocarbon waxes and resins to 15% by weight. The product was routinely under the 100 ppm (C6 – C9) limits and 5000 ppm total petroleum hydrocarbon limits. Separated oils were sent back to oil field distillation unit for reuse. Feed rate was 12 tph. Figure 1 shows aerial view and Figure 2 shows the indirect fired desorber.

Figure 1, Brunei Aerial View (Courtesy ASTEC)

Figure 2, Brunei ASTEC Indirect Desorber (Courtesy ASTEC)

Raleigh North Carolina, USA -- PCBs

System Owner/Operator: WRSCompass Environmental (Thermal Treatment Scope)

System Type: Counter current direct fired desorber, baghouse, oxidizer, wet quench, acid gas absorber

Site and Issues: Ward Transformer was an electrical transformer service facility constructed in 1964 on approximately 11 acres near the Raleigh-Durham Airport in Wake County, NC. In 2005 a multiparty trust and the USEPA signed a Settlement Agreement under the Comprehensive Environmental Response, Contribution, and Liability Act (CERCLA, aka Superfund) for a Removal Action at the Ward Site addressing polychlorinated biphenyls (PCBs). This project was a hybrid in that low concentration soil and debris and some high concentration soil and debris was shipped offsite for disposal, while higher PCB concentration soil was treated in the low temperature thermal desorption (LTTD). This hybrid approach led to a lower total cost compared with onsite treating the low concentration soil. TMTS provided support for the thermal processing task, visiting the site, reviewing soil data, writing the thermal services vendor spec, attending public meetings, meeting directly with local authorities, ranking bidders, reviewing test data and assisting on fuel use and costing. At the time of bidding the estimated volumes of soil to be addressed, based primarily on Remedial Investigation information provided by EPA, were:

LTTD treatment of soil with ≥ 50 mg/L (ppm) PCBs	65,200 tons
Off-site disposal of soil and debris with ≥ 50 ppm PCBs	2,000 tons
Off-site disposal of soil and debris with < 50 ppm PCBs	29,100 tons
Total	96,300 tons

Collection of additional data from thousands of samples during the Removal Action as required by the Settlement Agreement led to significant lateral and vertical and expansion of the Removal Action area. The final cleanup volumes[3] were:

LTTD treatment of soil with ≥ 50 mg/L (ppm) PCBs	304,712 tons
Off-site disposal of soil and debris with ≥ 50 ppm PCBs	28,530 tons
Off-site disposal of soil and debris with < 50 ppm PCBs	89,239 tons
Total	422,281 tons

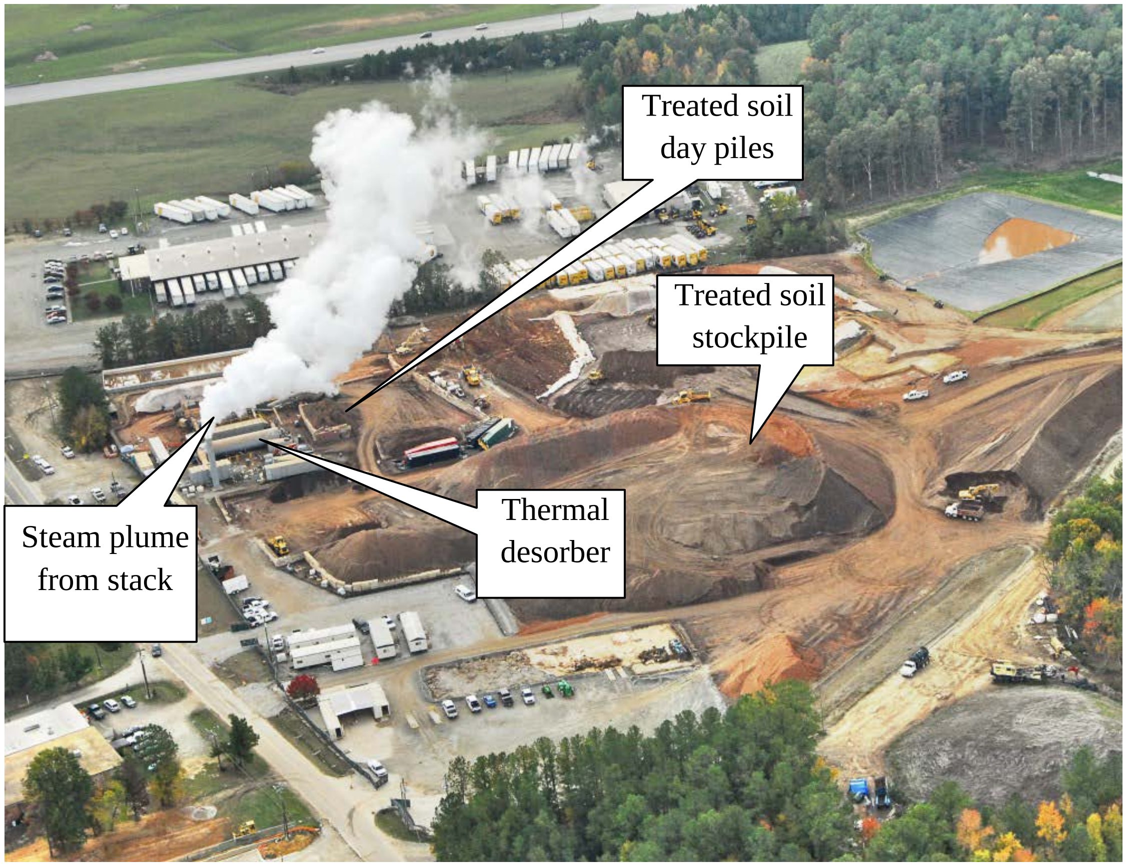
The area contained loamy silty soil, with silts presenting a challenge to prevent dusting of the hot treated product. Figure 3 shows an aerial view of the site and soil stockpile. EPA documents showed up to 1.3% (13,000 ppm) PCBs in isolated locations, making mixing with lower concentration material an important goal for soil from those areas. The usual challenge with PCB sites is need for high temperatures to achieve more than 99.9999% DRE, and with the countercurrent system used at WARD, keeping organic feed concentrations of high boiling point organics low and baghouse temperatures high to prevent the high boiling point organics from condensing in the baghouse. The system passed stack test on particulates, HCl, PCBs and dioxins (Table 3). The oxidizer was run at 1890°F (1032°C) during the production run, and given the almost eight 9's DRE test result, this temperature was perhaps overly conservative. Production run was just over 31 tph feed rate. The total cost was $62.3 million (~$148/ton) including engineering costs for Golder Associates, the remedial engineering and oversight firm hired by the Ward Transformer Superfund Site Trust.

Table 3, Stack Test Results

Parameter	**Performance Standard**	**#1**	**#2**	**#3**
Particulates	≤ 0.08 gr/dscf	0.008	0.004	0.007
Carbon	≤ 100 ppm_v	0.41	0.38	0.45
Combustion Efficiency	≥ 99.9%	99.9996%	99.9996%	99.9996%
Nitrogen Oxides	≤120 lb/hour (54kg/h)	9.18 4.2	9.25 4.2	8.52 3.9
HCl and Chlorine	> 99% HCl removal or≤ 4 lb/hr HCl (1.8 kg/h) or Cl2	0.05 lb/hr (0.02kg/h) <5.9E-04 lb/hr (0.00027 kg/h)	0.02 lb/hr (0.009 kg/h) 0.01 lb/hr (0.005 kg/h)	0.09 lb/hr (0.04 kg/h) <5.2E-04 lb/hr (0.0002 kg/h)
PCDD/PCDF	<0.4 ng/dscm (a)	0.03	0.03	0.03
Destruction and Removal Efficiency via Mono-Chlorobenzene Surrogate	≥99.9999%	99.999998%	99.999996%	99.999997%
PCBs in product soil	1 mg/kg	0.069	0.068	0.060
2,3,7,8 TCDD TEQ in product soil	1 μg/kg TEQ	0.348 J	0.261 J	0.262 J

Notes: Total tetra- through octa- chlorinated PCDD/PCDF, corrected to 7% oxygen, TEQ Basis (dioxin toxicity equivalence). J values are estimated

Figure 3, Ward Site Aerial Photo (Courtesy Golder Associates Inc.)



Utah, USA –Energetic/Explosive Waste

System Owner/Operator: ESMI of New York

System Type: ASTEC Cocurrent direct fired desorber, oxidizer, dry bottom quench, baghouse (see plant PFD in Figure 4)

Site and Issues: This was a cleanup at an ongoing energetic (explosives) materials manufacturing facility. The system processed approximately 91,000 tons of soils with no incidents related to the energetic material processed.

Soils contained low levels of explosive constituents RDX, PETN, TNT, and HMX. The project had a 100% success rate in achieving the risk-based processed soil cleanup criteria, and about 90% of the processed soils were below detection limits for residual energetics concentrations. This is not a surprising result, as energetics decompose rapidly at moderate temperatures

A critical aspect was feed preparation and mixing of soils to less than 2% by weight energetic material to ensure that the material was non-detonable (see Figure 5).

In addition to the soil, 55 cubic yards of pure nitrostarch product (an energetic material, similar to nitrocellulose) present at the remediation site was introduced to the LTTD unit during the project, successfully processed. The thoroughly wetted nitrostarch, packed in linin bags, was metered into the system, according to a specific site protocol, with a maximum batch weight of 5 pounds per drop.

Energetic constituents do not require high temperatures, and the desorber ran at an average hourly temperature of about 680°F (360°C) and a processing rate of up to 40 tons per hour. While the oxidizer was operated at 1,500°F (816°C), this treatment step is probably unnecessary for the energetic constituents which are effectively decomposed in the desorber.

The POP (proof of performance) test showed that all energetic material was below detection limits in the stack. VOCs were less than 0.003 lb/hr (0.0014 kg/hr), and semi volatiles were less than VOCs. Particulates were found to be somewhat elevated on the initial stack test due to broken bags in the baghouse; this was easily fixed. Measured SO2 was approximately 1 lb/hr (0.45 kg/h) Measured NOx was approximately 130 lb/hr (59 kg/hr) on the soils with higher energetic material concentrations used in the POP test (the system was not equipped with SCR or other NOx reduction APC), but dropped significantly during the production run when lower energetic concentration was the rule.

Cost of excavation, soils management and thermal treatment were less than $100/per ton exclusive of analytical work. More detail can be had in reference 4.

Figure 4, Low Temp Desorber Used for Soil Contaminated with Explosives[4]

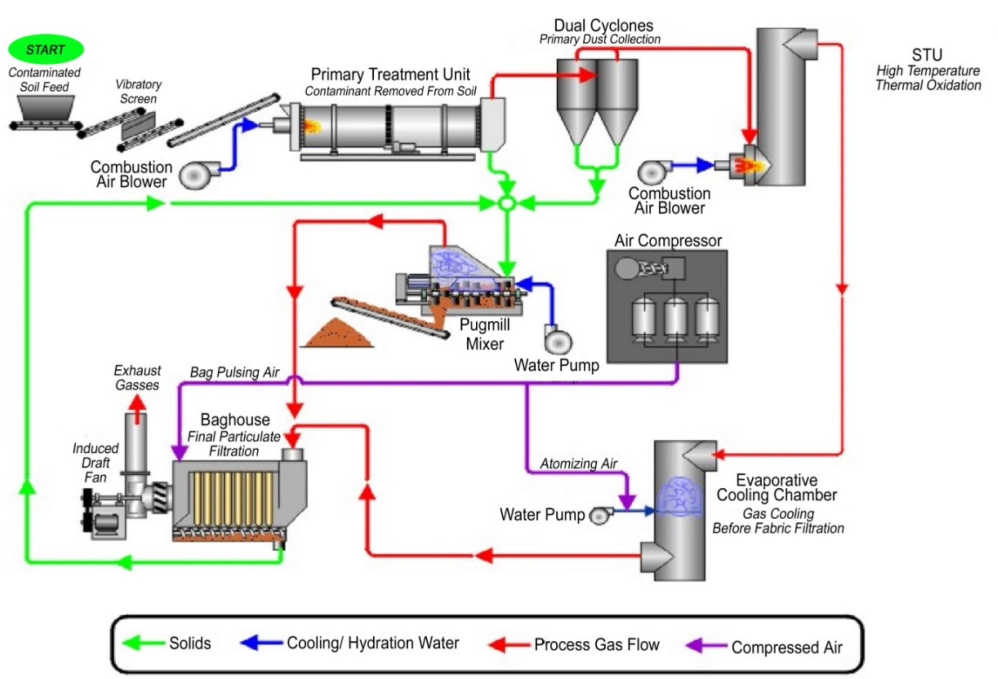
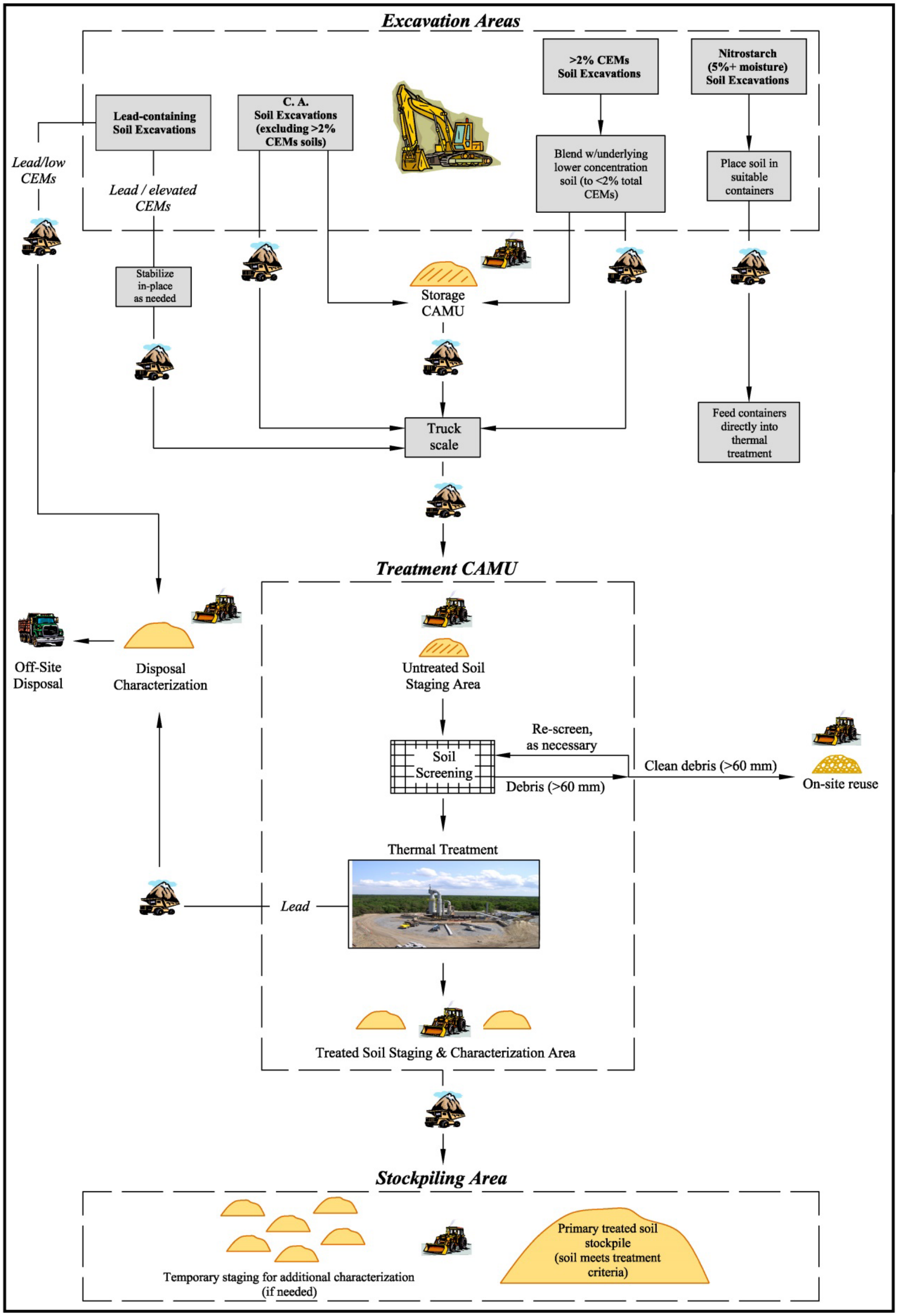


Figure 5, Onsite Soil Management Scheme[4]



Antwerp, Belgium – Heavy Hydrocarbons

System Owner/Operator: Envisan (Belgium)

System Type: Tarmac direct fired rotary desorber, countercurrent with cyclone, oxidizer, primary and secondary heat exchanger, baghouse.

Site and Issues: The site had a fire, which resulted in soil contaminated with heavy hydrocarbons and small plastic pellets. Hence, the primary issue was getting the product hot enough to remove the high boiling point material. Figures 6 and 7 show the process flow diagram, aerial site view and equipment layout.

Figure 6, Antwerp Process Flow Diagram (Courtesy Tamac)

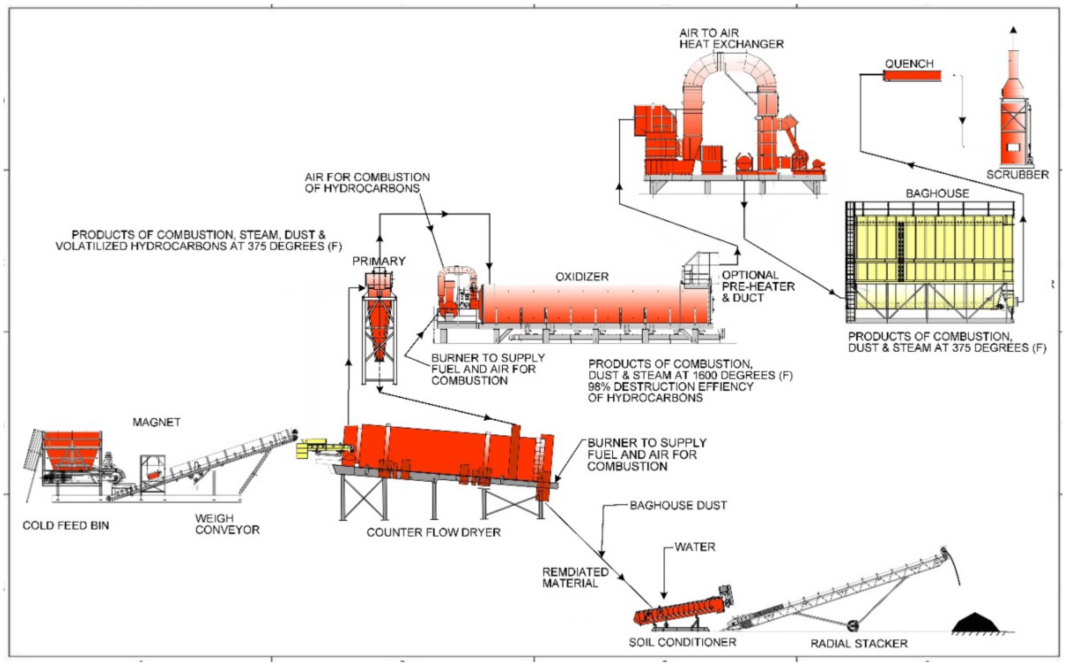


Figure 7, Aerial View of Direct Fired Desorber System (Courtesy Tarmac)

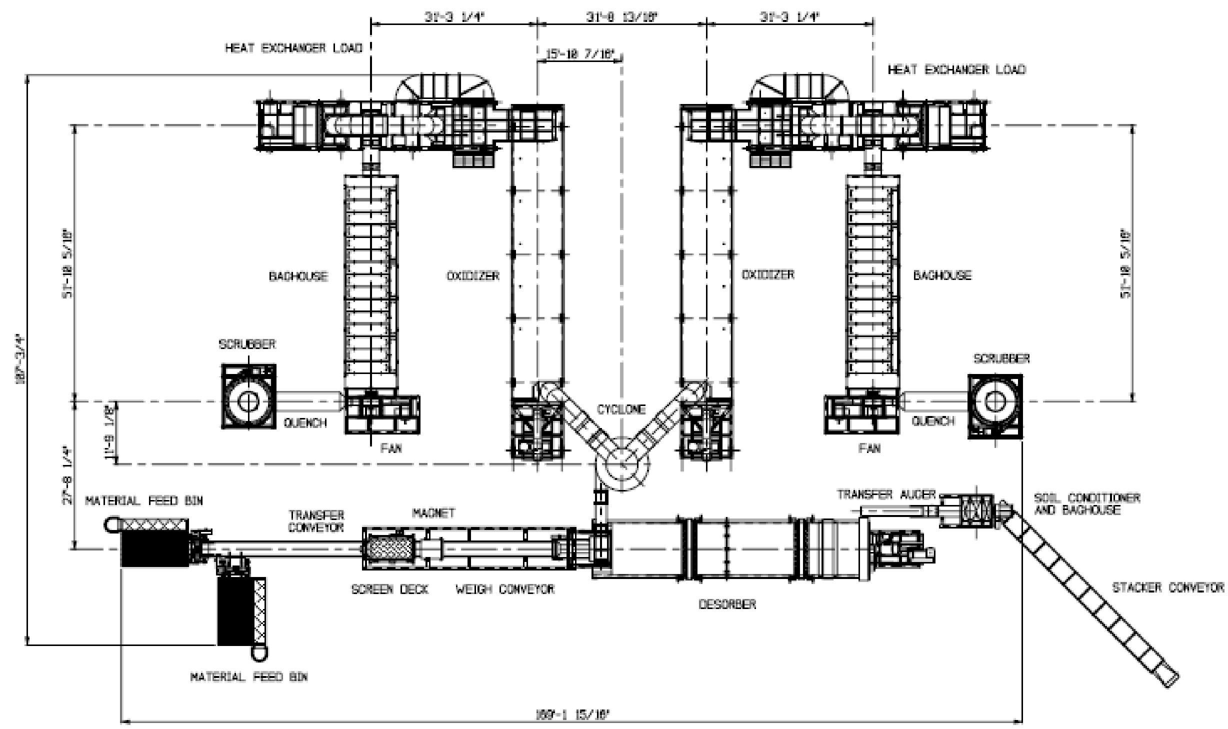
Brasi, Romania - Refinery Waste

System Owner/Operator: Recon LP, Houston, TX

System Type: Tarmac countercurrent direct fired rotary desorber, cyclone, oxidizer, primary and secondary air-to-air HX, baghouse with lime injection, acid gas scrubber. See Figure 8 for plant layout.

Site and Issues: The site is an oil refinery. Petroleum wastes were processed. Feedstock was soil with about 2.5% TPH (total petroleum hydrocarbons). The desorber product passed tests at less than 25 mg/kg (ppm) petroleum. The average value of stack test results for NOx, CO, and HCl was at or below about $1/10^{th}$ the applicable limits.

Figure 8, Brasi Refinery Plant Layout (Courtesy Tarmac)



Princeton B.C. Canada – Tank Bottom Mix

System Owner/Operator: Envirogreen

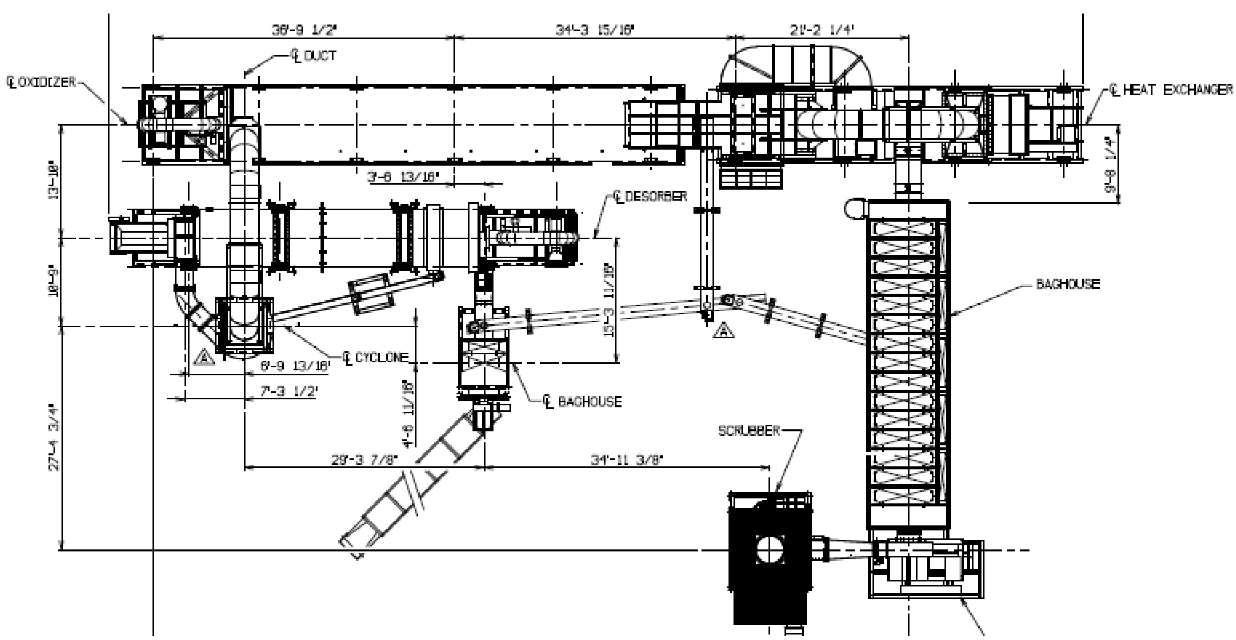
System Type: Tarmac Direct fired rotary desorber, cyclone, oxidizer, air to air HX, baghouse, SO2 scrubber

Site and Issues: The system runs at 30-35 tph. Table 4 shows stack tests results, all well below applicable limits. The waste is petroleum tank bottoms, mixed with low level organic concentration waste prior to feeding. The feedstock contained sulfur, and the resulting SO2 is removed via a caustic acid gas scrubber. Figure 9 shows the plant layout.

Table 4, Princeton B.C. Canada Envirogreen Stack Test Results (Courtesy Tarmac)

Parameter	**06 June 2013 Test @ 11%O2**	**Limit @ 11% O2**
PM mg/Sm3	4.4	20
NOx as NO2 mg/Sm3	106	380
SO2 mg/Sm3	8.4	180
THC as methane mg/Sm3	1.4	32
CO mg/Sm3	26.8	55
Combustion Eff. %	>99.9	>99.9
DRE %	99.994	>99.99

Figure 9, Envirogreen Plant Layout



SUMMARY

Many thermal treatment projects have been successfully executed. To do so simply requires testing and knowledge of soil properties and contaminants, a proper match between the desorber and air pollution control equipment and the waste, and appropriate project objectives.

REFERENCES

1. McGowan, Thomas F., Remediating Organic-laden Soils: Do Your Homework Before Breaking Ground," Chemical Engineering Magazine, 4/2/2004
2. UNEP/POPS/EGB.1/INF/10, 1/27/03, Formation of PCDD and PCDF – an overview2; Stieglitz *et al.* 1989
3. Removal Action Completion Report, submitted to USEPA, Phase 1, June 2012
4. Low Temperature Thermal Deactivation for Remediation of Energetic Materials in Soil, IT3 Conference, May 14-18, 2007, Phoenix, AZ, Thomas F. McGowan; Philip Theriault; and Mark Franson

ACKNOWLEDGMENTS

Gary H. Collison, Practice Leader and Principal, Golder Associates, Tucker, GA for contributions on the Ward Transformer Site case study

GLOSSARY

EPA: United States Environmental Protection Agency. DRE: Destruction and Removal Efficiency -- based on mass in of an organic contaminant vs. mass out the stack. LEL: Lower explosion limit. OEMs: Original Equipment Manufacturers. PCBs: Polychlorinated biphenyls -- used as transformer oils and for other applications. PFD: Process flow diagram. SCR: Selective catalytic reduction; SNCR: Selective non-catalytic reduction, both for reducing nitrogen oxides.

KEYWORDS

Thermal treatment, contaminated soils, explosives, energetic material, PCBs, dioxins, air pollution control, remediation, desorption