Scaling up of Dioxin Contaminated Soil Thermal Desorption Treatment: Laboratory tests and pilot conception at Bien Hoa Airbase, Vietnam

A. JORDENS[1], H. SAADAOUI[2], J. HAEMERS[3]

Introduction

During the US-Vietnam War, millions of litres of herbicides were dropped over Vietnam: The Rainbow agents. Those Rainbow Agents were sprayed throughout the Operation Ranch Hand to clear thick jungle, by defoliating crops and forest. Bien Hoa Airbase was a joint operating base for the South Vietnam Air Force and the United States Air Force. According to the U.S. Department of Defense, 98 000 barrels (208 L) of Agent Orange, 45 000 of Agent White and 16 000 of Agent Blue were stored at Bien Hoa Airbase [1]. Nowadays, between 408.500 and 495.300 m³ of dioxin-contaminated soil and sediment at Bien Hoa Airbase are estimated [2].

Agent Orange was proven to cause severe health issues, including birth defects, neurological problems and cancers. Agent Orange is a mixture of 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic. Traces of dioxins were also found in some Agents. Indeed, dioxin 2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) can be formed by condensation of 2,4,5-trichlorophenol during 2,4,5-trichlorophenoxyacetic synthesis.

Dioxins are highly toxic environmental persistent organic pollutants. As their toxicity is very variable, a toxic equivalency factor (TEF) has been developed: the reference compound being the 2,3,7,8-tetrachlorodibenzo-p-dioxin t2,3,7,8-TCDD, which has a TEF of one. The Toxic Equivalent Quantity (TEQ) characterizes the toxicity of a mixture of dioxins and dioxin-like compounds as it was the most toxic dioxin, the 2,3,7,8-TCDD.

More than four decades after the Vietnam War ended (in 1975), the stability and bioaccumulation of dioxins still affect the inhabitants. Measures had to be taken to improve living conditions for residents, starting with the remediation of dioxin contaminated soil.

An Environmental Assessment of Dioxin Contamination has been launched at Bien Hoa Airbase in order characterize dioxin contamination and its remediation [2]. There are several remediation technologies that can be applied to treat dioxin contaminated soil. Thermal desorption has already been identified as an effective method for cleaning up those soil. Indeed, a thermopile of 45.000 m³ has been established at Danang Airport, another major Vietnamese airbase contaminated with dioxins. Results showed that the treatment has successfully met the clean-up goals [3].

A pilot of *In Situ* Thermal Desorption (ISTD) and *Ex Situ* Thermal desorption (ESTD) will be conducted by HAEMERS Technologies © at Bien Hoa Airbase in 2019., in partial combination with soil washing. This paper describes the laboratory tests that have been completed, the design of the thermal remediation installation and the vapor treatment unit that will be in operation on site.

Laboratory tests

Contaminated soil from the Bien Hoa Airbase has been sent to HAEMERS Technologies' laboratory in Belgium to be tested in a lab-scale thermal desorption unit. The purpose of the test is to validate the thermal desorption technology for dioxin contaminated soils. Samples are analysed and compared before and after treatment.

The heating phase is carried out in a thermally insulated metal container. The soil is heated inside the latter by an electric resistance located in the center of the container. The electrical resistance is controlled by a temperature controller in the ON / OFF mode, which allows the temperature of the resistor to be set to reach the target temperature. A perforated vapor tube, designed to collect the polluted vapours created by heating,

[1] HAEMERS Technologies SA, aline.jordens@haemers-tech.com
[2] HAEMERS Technologies SA, hatem.saadaoui@haemers-tech.com
[3] HAEMERS Technologies SA, jan.haemers@haemers-tech.com

 © HAEMERS Technologies 2019

is located at about 7cm from the resistance. The vapor tube is connected to a refrigerant in serpentine condensing the vapours which are recovered in a round-bottom flask. A fan creates the negative pressure in the vapor network and blows the remaining vapors into the activated carbon filters before the exhaust in the atmosphere.

The evolution of the temperature in the soil is monitored using several K-type thermocouples placed in the soil sample at various positions. The treatment is stopped after 138 hours at a resistance temperature of 600 °C maintained for 19 hours. The soil temperature slightly increased over time to reach 314°C at the coldest points.

Samples are collected and sent to an aggregated soil analysis laboratory. The initial state is given by the non-treated samples. The results are shown in the Table 1:

	Contaminated sample	*Treated sample*	*Unit*
Dry matter	94,9	99,7	% (dry matter mass)
2,3,7,8-Tétra CDD	2800	630	ng/kg DM
1,2,3,7,8-PentaCDD	14	84	ng/kg DM
1,2,3,7,8,9-Hexa CDD	13	27	ng/kg DM
1,2,3,6,7,8-HexaCDD	20	42	ng/kg DM
1,2,3,4,7,8 -Hexa CDD	3,5	7,5	ng/kg DM
1,2,3,4,7,8,9-Hepta CDD	99	46	ng/kg DM
Octa CDD	450	200	ng/kg DM
1,2,3,7,8 Penta CDF	1,7	3,2	ng/kg DM
2,3,4,7,8-Penta CDF	1,2	2,8	ng/kg DM
2,3,7,8-Tétra CDF	75	28	ng/kg DM
1,2,3,7,8,9 - Hexa CDF	<1,0	<1,0	ng/kg DM
2,3,4,6,7,8 - Hexa CDF	2,3	1,9	ng/kg DM
1,2,3,4,7,8 Hexa CDF	1,5	2,0	ng/kg DM
1,2,3,6,7,8 Hexa CDF	<1,0	1,4	ng/kg DM
1,2,3,4,7,8,9 -Hepta CDF	<5,0	<5,0	ng/kg DM
1,2,3,4,6,7,8 -Hepta CDF	9,4	<5,0	ng/kg DM
Octa CDF	<10	<10	ng/kg DM
I-TEQ-PCDD/F-OTAN/CCMS (lower limit)	2820[4]	685	ng/kg DM
I-TEQ-PCDD/F-OMS 1998 (lower limit)	2830[4]	727	ng/kg DM
I-TEQ-PCDD/F-OMS 2005 (lower limit)	2830[4]	726	ng/kg DM
I-TEQ-PCDD/F-OTAN/CCMS (upper limit)	2820[5]	685	ng/kg DM
I-TEQ-PCDD/F-OMS 1998 (upper limit)	2830[5]	727	ng/kg DM
I-TEQ-PCDD/F-OMS 2005 (upper limit)	2830[5]	727	ng/kg DM

Table 1. Analysis of soil before and after treatment

[4] The results do not take into account the contents of the quantification thresholds
[5] For each individual result below the DL, the DL is used for the calculation, for each individual result between the DL and the LQ, the LQ is used for the calculation

© HAEMERS Technologies 2019

We observe an important decrease of TEQ-PCDD (Poly-chlorodibenzo-*p*-dioxins) from approximatively 2800 to 600-700 ng/Kg DM before and after the treatment respectively. The amount of 2,3,7,8-TétraCDD has been reduced by 77,5%. A longer treatment time once the target temperature achieved, would allow achieving a higher contaminants reduction.

These results report that for the dioxins and furans, thermal desorption treatment can ensue efficient outcomes. Treating the soil at +/-350°C and maintaining this temperature during at least 5 days reduces the TCDD concentrations by 77,5%.

<u>Process: Smart Burner™ Technology</u>

Smart Burner™ by HAEMERS Technology© is a technology suitable for a wide range of pollutants. The technology involved two stages: the heat of the soil by conduction and the vapor extraction by aspiration.

Its implementation requires little equipment. The process involves drilling holes in the contaminated area and putting heating tubes and vapor tubes in them. Thanks to the burners, the tubes heat the soil until the temperature required for the desorption of the pollutants is reached. During the treatment no contact occurs between the heating gas and the contaminated soil.

The vapours are collected through the vapor tubes, which are perforated. The negative pressure in the tubes is created by a Vapor Treatment Unit, where the vapours are treated. On this specific case, vapours are thermally oxidized in order to definitively destroy all dioxins, furans and associated pollutants.

<u>Pilot design</u>

Following the promising results of the laboratory experiment, a pilot project has been designed. It has been decided to treat in two different layouts: one *Ex Situ Thermal Desorption* (ESTD) and one *In Situ Thermal Desorption* (ISTD).

The ISTD design is composed of 48 vertical heating tubes (figure 1a). The area to be treated is a 10 by 10-meter square (100m²) of 2 meters depth. HAEMERS Technologies©' burners are diesel burners: combustion gas circulate though the inner and the outer tubes to heat the soil by conduction. Each heating tube is adjacent to a vapor tube (collecting the contaminated vapours produced by the heating). Those vapor tubes are connected to two collectors which are joined to a main collector leading the polluted vapours to the Vapor Treatment Unit (VTU). The ISTD will be conducted in a landfill area, where contaminated soils have been stored and restrained over the years. The soil concentration limits after treatment have been defined as following [2]:

- Industrial use: 1.200 ppt
- Urban area: 300 ppt
- Sediment: 150 ppt

The ESTD is composed of 11 horizontal heating tubes and 4 exchanger tubes (figure 1b). The exchanger tubes collect the combustion gas after passing through the pile and allow a second pass through it. The sixteen vapor tubes placed inside the pile are connected to a collector leading the polluted vapours to the VTU.

The 500 tons pile's origins are diverse: 200 tons are contaminated soils, 200 tons are contaminated sludges and 100 tons are washing cake. Soil washing is a remediation technique using physical separation technique to remove contaminants from soils. Particles are separated by size. As a matter, most contaminants tend to be sorb to clay and silt. Washing separates those small particles from larger ones (sand and gravel) by breaking adhesive bonds and by mean of filtration. A contaminated filter-cake residue results from this technique. To avoid the landfill disposal of this residue, the cake is treated in the ESTD pile.

 © HAEMERS Technologies 2019

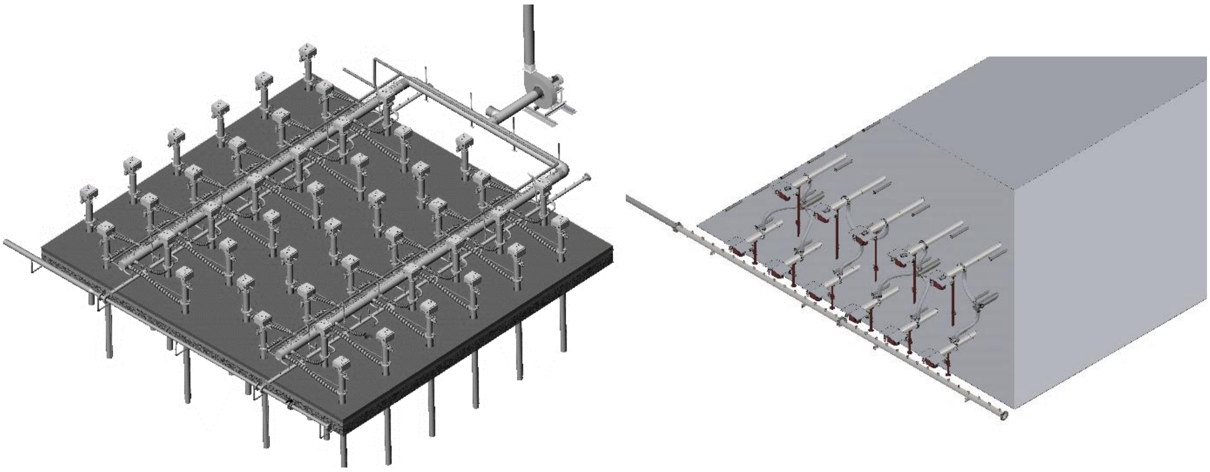

Figure 1 (a, b) – ISTD design (left) and ESTD design (right)

Vapor treatment

The purpose of the VTU (Vapor Treatment Unit) is to handle the contaminated vapors produced in the soil and reduce their concentrations below legal emission standards. Two main options are available: Condensation and Absorption on Activated Carbon or Thermal Oxidation [4].

The main advantage of the first option is the low energy consumption. Nevertheless, liquid and solid waste are produced: the liquid obtained after condensation must be post-treated and the activated carbon must be disposed as a hazardous waste.

On the other hand, using a Thermal Oxidizer allows to avoid any liquid/solid waste. The vapors are directly incinerated in order to destroy all PCDD and PCDF's. Proper oxidation guarantees compliant air emissions. It has to be noted that condensation will certainly happened along the network. To reduce liquid formation, the network is isolated. Nevertheless, the liquid formed can be reinserted in the Thermal Oxidizer. To reach a destruction rate efficiency over 99,99%, the following criteria must be fulfilled in the oxidation chamber [5][6]:

1. Temperature of minimum 1100°C (preferably 1200°C)
2. Oxygen content of min 6% (preferably 10%)
3. Residence time of minimum 1 second (preferably 2 seconds)
4. High Turbulence (Re>>2500).

It is well known that dioxin compounds reformation can happened in the cooling phase, in a temperature range between 200°C and 500°C. Dioxins can be reformed in the presence of oxygen, chlorine (Cl_2) and hydrocarbons [7]. Other parameters such as presence of dust and/or presence of metals, can also promote the dioxins/furans formation. To avoid the reformation process, the vapors are directly released into the atmosphere after oxidation, leading to a fast cooling far below 200°C.

Conclusions

Nowadays, Vietnam is facing a major issue regarding quantities of dioxins/furans contaminated soils. Indeed, those remnants of the US-Vietnam war are affecting the quality of life of the inhabitants.

Thermal desorption is a technology that has been proven effective for dioxins/furans contaminated soils remediation. Laboratory tests have shown a high contaminant reduction rate after thermal treatment: treating the soil at 350°C for 5 days reduces the Poly-chlorodibenzo-*p*-dioxins by 77,5%. A higher reduction rate could certainly be reached with a few of more days at this temperature.

The pilot project has been designed according to the laboratory tests conclusions. One ISTD (*In Situ* Thermal Desorption) and one ESTD (*Ex Situ* Thermal desorption) are planned to be installed at Bien Hoa Airbase,

© HAEMERS Technologies 2019

Vietnam. The ISTD will take place in a landfill area, where tonnages of contaminated soils have been accumulated over the years, while the ESTD pile will contain 100 tons of cake from soil washing.

The choice of the Vapor Treatment Unit has been based on HAEMERS Technologies© experience and to avoid residual waste production. Thermal Oxidizer is the preferred of the two options available for treating the vapours. The process designed for this project insure a 99,99% Destruction Rate Efficiency for dioxins and furans, with no reformation possibility.

References

[1] DOD. 2007. Presentation made at the Second Agent Orange and Dioxin Remediation Workshop, Hanoi, Vietnam, June 18-19, 2007. Co-sponsored by U.S. Department of Defense and Vietnam Ministry of National Defense.

[2] USAID. 2016. Environmental Assessment of dioxin contamination at Bien Hoa Airbase

[3] USAID. 2015. Vietnam: Environmental Remediation of Dioxin Contamination at Danang Airport – Progress Report: April 1, 2015 to June 30, 2015.

[4] HAEMERS J., SAADAOUI H. Treatment of Dioxin impacted soils by Ex Situ Thermal Desorption – How to handle vapors

[5] Gao, Y. &. (2015). Assessment of Reynolds Averaged Navier–Stokes Modeling of Scalar Dissipation Rate Transport in Turbulent Oblique Premixed Flames. Combustion Science and Technology, 18

[6] Jacob E. Temme, T. M. (2015). Measurements of Premixed Turbulent Combustion Regimes of High Reynolds Number Flames. 53rd AIAA Aerospace Sciences Meetin (p. 21). Kissimmee, Florida : AIAA SciTech Forum.

[7] Buekens, A. (2001). Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry,. Chemosphere 42, 729-735.

© HAEMERS Technologies 2019