



Interaction of soil, water and TNT during degradation of TNT on contaminated soil using subcritical water

Dimitrios Kalderis^{a,*}, Steven B. Hawthorne^b, Anthony. A. Clifford^c, Evangelos Gidarakos^a

^a Technical University of Crete, Department of Environmental Engineering, University Campus, 73100 Chania, Crete, Greece

^b Energy and Environmental Research Center, University of North Dakota, 58202 Grand Forks, Campus Box 9018, USA

^c School of Chemistry, University of Leeds, LS2 9JT Leeds, United Kingdom

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ABSTRACT

Subcritical water was used at laboratory scale to reveal information with respect to the degradation mechanism of TNT on contaminated soil. Highly contaminated soil (12% TNT) was heated with water at four different temperatures, 150, 175, 200 and 225 °C and samples were obtained at appropriate time intervals. At the same time, similar experiments were performed with TNT spiked on to clean soil, sand and pure water in order to compare and eliminate various factors that may be present in the more complex contaminated soil system. Subcritical water was successful at remediating TNT-contaminated soil. TNT destruction percentages ranged between 98 and 100%. The aim of this work was to study the soil–water–contaminant interaction and determine the main physical parameters that affect TNT degradation. It was shown that the rate-limiting step of the process is the extraction/diffusion of TNT molecules from the soil core to the soil surface, where they degrade. Additionally, it was determined that the soil matrix also catalyses degradation to a lesser extent. Autocatalytic effects were not clearly observed.

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1. Introduction

TNT (2,4,6-trinitrotoluene, molecular weight, 227.1, solubility in water at 25 °C, 100–200 mg/L reported in literature) has been extensively used as a military explosive for more than 50 years. Although many novel explosive compounds have been developed, TNT is still one of the most widely used explosives in plastic formulations with other substances such as HMX and RDX. Fig. 1 shows the structure of TNT. Its success is due to the low manufacturing costs, safety of handling and high explosive power. The toxicity and mutagenicity of TNT to animals, fish, plants and microorganisms is well documented [1–3]. To humans, it is relatively toxic through inhalation, oral absorption and skin contact [4]. Some of the common symptoms of TNT toxicity are severe headaches, nausea, cyanosis and anaemia [3–4].

The long-term exploitation of TNT has resulted in large areas of contaminated soil and groundwater at processing and manufacturing sites, as well as military testing fields. Waste disposal procedures and destruction of out-of-date munitions have extended the problem. A study performed by the U.S. Army Cold Regions Research and Engineering Laboratory showed that TNT occurs in ca. 80% of the contaminated soil samples obtained from U.S. military sites [5].

Incineration is widely used for remediation of explosives-contaminated soil. It can effectively (99.9%) remediate soils contaminated with TNT and it is not affected by the presence of other explosives or debris in the soil. However, it is an expensive method that destroys the soil structure (ash is produced after treatment) and continuous monitoring of air emissions is required to ensure that toxic by-products are not released into the atmosphere [5–8]. Bioremediation methods such as composting and slurry-phase treatment can degrade TNT in a more environmentally friendly manner and are not as expensive as incineration. However, biological methods require longer times (weeks or even months) to degrade the contaminants and often during treatment more toxic by-products are produced [5,9–10].

Other methods used for treating TNT-contaminated soil include phytoremediation and reduction using zero-valent iron, however, both have serious limitations. Phytoremediation can only be applied to sites with low, near-surface contamination and monitoring of degradation and potential by-products is difficult [11]. Zero-valent iron reduction of TNT-contaminated soil requires the addition of considerable quantities of Fe to be effective [6].

Subcritical water is hot water (>100 °C) under enough pressure to maintain the liquid state. It is an environmentally friendly and inexpensive solvent that exhibits a wide range of properties that render it very effective in solvating and decomposing moderately polar or non-polar substances from a wide range of environmental matrices.

* Corresponding author. Tel.: +30 28210 37820; fax: +30 28210 37847.
E-mail address: dimitrios.kalderis@enveng.tuc.gr (D. Kalderis).

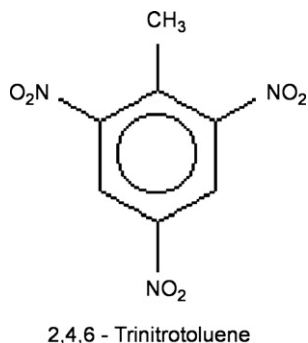


Fig. 1. Structure of 2,4,6-trinitrotoluene.

Several studies have shown that subcritical water can decompose naturally occurring substances and materials, such as complex amino acids [12], proteins and carbohydrates (sucrose, fructose and sorbose) [13–17], sodium alginate [18] and brown coal [19], to produce more valuable and useful products. Additionally, subcritical water has been proved to decompose hazardous organic substances and materials such as pentachlorophenol (PCP), fluorochemicals, dioxins, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polyvinyl chloride (PVC).

Hori et al. [20–21], investigated the decomposition of perfluorohexanesulfonate (PFHS) and perfluorooctanesulfonate (PFOS), in subcritical water at temperatures between 150 and 380 °C. They found that at 350 °C and 6 h residence time, PFHS concentration was reduced by 84.7% when 9.61 mmol of iron powder was added to the system. F^- , SO_4^{2-} , and CF_3H were formed as by-products. At the same conditions, PFOS was reduced to non-detectable levels.

Pentachlorophenol (PCP) is a well-known carcinogen. The hydrothermal decomposition of PCP was examined in a tubular reactor under sub- and supercritical water conditions with sodium hydroxide addition [22]. At the subcritical temperatures of 300 and 350 °C, approximately 30 and 40% destruction was achieved respectively, at a residence time of 70 s. Temperatures at the supercritical region proved to be more effective. Near-complete degradation (>99%) was achieved between 380 and 420 °C in less than 60 s residence time. Hashimoto et al. [23] studied the effectiveness of subcritical water extraction for removing and degrading dioxins from contaminated soil. After 4 h of extraction, 99.4, 94.5 and 60% of PCDDs were removed from samples at 350, 300 and 150 °C, respectively. It was also determined that degradation of dioxins had occurred, since the sum of dioxins in the soil plus water extracts after the experiments had considerably decreased. For example, the total amount of dioxins found in the aqueous extract at 300 °C was only 20% or less of the original amount.

Fang and Kozinski [24] studied the phase behavior and combustion of hydrocarbon-contaminated soil in subcritical and supercritical water, using a hydrothermal diamond anvil cell. Their results showed that 99.86% benzo(a)pyrene and 100% naphthalene were converted during 300 s reaction time at 450 °C, 30.6 MPa and 17.1 excess oxygen. They concluded that even residues with high ash content (~20%) and stable PAHs could become almost completely oxidized to CO_2 and H_2O under supercritical conditions. Using the same methodology the group managed to oxidize organic residues obtained from nuclear plants [25] as well as deca-chlorobiphenyl (10-CB, a known PCB). At 450 °C and 225% excess oxygen, 99.2% of 10-CB was destroyed in 1200 s. To minimize corrosion, the authors added Na_2CO_3 and then the 10-CB destruction rate increased to 99.7% at 93% excess O_2 [26]. When they added methanol to enhance the destruction rate of 10-CB, they managed 100% destruction at 450 °C in 10 min, without the use of excess oxygen. They showed that methanol promoted PCB decomposition

through the production of highly reacting free radicals. Compared to excess oxygen, methanol also leads to the formation of fewer by-products [27].

Yang and Hildebrand [28] studied the degradation of pure phenanthrene in subcritical water at temperatures ranging from 100 to 350 °C. They found that, without the addition of any oxidants, at 350 °C only 61.9% of phenanthrene was degraded, whereas, when 3% hydrogen peroxide was added, 100% degradation was achieved at the same temperature. They concluded that the main parameters affecting the subcritical water degradation of phenanthrene is the temperature and the initial concentration of the substance.

Polyvinylchloride is a plastic material widely used in domestic power and lighting applications, car wiring, switchboards and telephone leads. When disposed of, phthalates and heavy metals can leach into the soil and groundwater. Takeshita et al. [29] investigated the decomposition of PVC by sub- and supercritical water. At 300 °C, chlorine in PVC dissolved in water as hydrochloric acid, and no harmful chlorinated organic compounds were observed in the liquid and gas fractions after treatment. At subcritical conditions, polyene was produced as a residual solid. Low-molecular weight aromatic and aliphatic compounds were determined in the liquid and gas fractions. Further decomposition at over 350 °C in supercritical water produced acetone, phenol, benzene, benzene derivatives, and aliphatic alkane and alkene in the liquid and gas fractions. Waste polymers such as polycarbonates have been efficiently decomposed by Tagaya et al. [30] using subcritical water at 300 °C. At 2 h residence time, polycarbonate degradation yielded ~65% phenol, when Na_2CO_3 was added to accelerate the process.

In our previous work [31], the pilot-plant scale destruction of TNT, HMX and RDX on contaminated soil using subcritical water under non-oxidative conditions, was studied. As far as TNT is concerned, it was found that near complete (>99.9%) degradation was achieved at 250 °C and 30 min residence time. The results from the pilot-plant scale experiments agreed well with those obtained at laboratory-scale. When the contaminated soil was heated at 275 °C for 1 h, in the presence of water, >99% destruction of TNT was achieved. Similar results were obtained with respect to HMX and RDX.

This study examines the degradation of TNT at lower temperatures, namely 150, 175, 200 and 225 °C and attempts to bring an insight on the soil–water–contaminant interactions of TNT degradation on soil by subcritical water. The use of subcritical water reactions without oxidants is largely unstudied and therefore the role of the soil matrix under these conditions is not well understood.

2. Experimental

2.1. Soils

TNT-contaminated soil was from a Ministry of Defense site in the United Kingdom and contained 12 wt % ($120,000 \pm 10,000$ mg/kg) of TNT but no significant levels of other explosives. It was mixed for 2 h in a concrete mixer to ensure homogeneity [18].

Concentration of TNT was based on the analysis of eight 2-g subsamples of the homogenized bulk soil sample. An uncontaminated agricultural soil (obtained locally) was used for spiking experiments. Particle size distributions and water contents for the TNT-contaminated soil and the agricultural soil are shown in Table 1.

2.2. Subcritical water apparatus

One type of small laboratory reactor was used for the degradation studies. The 5 mL reactors for 2-g samples were constructed from 77-mm long, 7-mm i.d. (12-mm o.d.) 316 stainless steel pipe

Table 1

Particle size distribution and water contents of the TNT-contaminated soil and the agricultural soil

	TNT contaminated soil (%)	Reference soil (%)
<0.125 mm	20	15
0.125–0.25 mm	19	12
0.25–0.5 mm	19	28
0.5–1 mm	23	20
1–6 mm	19	25
Water content	14	6

with national pipe threads (npt) and end caps sealed with Teflon tape [32]. These cells were loaded with 2 g of soil and 2 mL of HPLC-grade water and capped. Water had been purged with nitrogen to remove dissolved oxygen, to ensure that degradation is performed under non-oxidative conditions. This ensures that the toxic by-products formed during oxidative approaches such as wet air oxidation, supercritical water oxidation and bioremediation are avoided. The handling and preparation of the cells was performed in a fume cupboard under an Argon atmosphere.

This procedure left ca. 1.5 mL of headspace in the cell. Cells were placed in a (pre-heated at the required temperature) GC oven (Hewlett-Packard 5890, series II) for heating. Each of the cells was removed from the oven at appropriate time intervals, allowed to cool to room temperature. The resultant slurry was centrifuged and the soil (or sand) and water phases were recovered separately for analysis. All experiments were carried out in triplicate and error bars were added to the figures accordingly.

Safety note: All static (nonflowing) reaction vessels must contain a sufficient headspace so that the pressure inside the vessel is controlled by the steam/liquid equilibrium. A full vessel must never be used since the pressures could reach several thousand bar [33].

2.3. Analysis

All untreated soils, treated soil residues, and wastewaters from every degradation experiment were analyzed using EPA method 8330. To determine the concentration of TNT on the contaminated soil, the soil was extracted with acetonitrile by sonication for 18 h, and the water sample was diluted 1:1 in acetonitrile before analysis by HPLC with UV detection (HPLC/UV) at 254 nm with isocratic elution with 82/18 water/2-propanol [18]. The same dilution was used for the subcritical water extractions. Solvent programming from 85/15 water/methanol to 100% methanol was used to obtain higher resolution in order to analyze selected samples for intermediate products. All separations were conducted with a Waters HPLC (model 2487 dual wavelength UV-vis detector, and model 515 pump) equipped with a “Nova-Pak” C-18 HPLC column (15 cm long, 4 mm i.d., with 4 μm packing). Peak identifications and quantitations were based on the injection of known compounds.

2.4. Recovery experiments for TNT spiked on to sand and reference soil

The maximum levels of TNT that could be recovered from sand and the reference soil after spiking at room temperature were tested, using 1000 μg of explosive substance spiked on 1 g of sand and reference soil respectively. This test was performed to determine whether some of the explosive compound spiked on a reference matrix is lost before the start of the experiment. In this way it is possible to determine the ‘realistic’ maximum concentrations to be expected when analyzing the water and soil phases after the spiked degradation experiments are carried out. After spiking, the solvent was allowed to evaporate for ~15 min. Then water was

Table 2

Recovery results for TNT spiked on to sand and reference soil

	Sand	Reference soil
% TNT in water	98	90
% TNT in solid matrix	2	9
Total (%)	100	99

added and the extraction vessels were mechanically shaken for 15 min and the two phases were finally separated and analyzed. The experiment was performed at ambient conditions. The results are shown in Table 2.

3. Results and discussion

3.1. Recovery results for TNT spiked on to sand and reference soil

After ~30 min, the distribution of TNT in the solid and water phase is comparable between sand and reference soil. The majority of TNT molecules are found in the water phase, indicating that the degree of sorption on each of the solid matrices is very low.

3.2. TNT degradation on historically contaminated soil

The degradation kinetics of TNT were studied at four different temperatures, 150, 175, 200 and 225 °C. Fig. 2 shows the results for TNT degradation on contaminated soil at the above temperatures. At 150 °C, 99.6% degradation of TNT is achieved in 420 min. In the first 30 min TNT degrades slowly, then follows a faster rate until 210 min and after that degradation continues more steadily to the end-point of 420 min.

At 175 °C, a similar trend is observed. Degradation is initially slow, the rate is then increased and finally slows down again until 100% destruction is achieved in 240 min. At 200 °C, 100% destruction is achieved in 90 min. At 225 °C, complete (100%) degradation of TNT is achieved in 20 min.

It is very important to note that small concentrations of TNT are detected in the water phase in comparison with the soil phase, after treatment. As shown in our earlier work [18], this may be due to the fact that solvated, undegraded TNT molecules return to the soil upon cooling or the molecules once diffused from the soil matrix and solvated, they degrade.

Fig. 3 shows the times required to achieve 100% degradation of TNT at different temperatures. The times are in good linear agreement, enabling us to predict complete TNT degradation times at temperatures in the range of 100–150 °C.

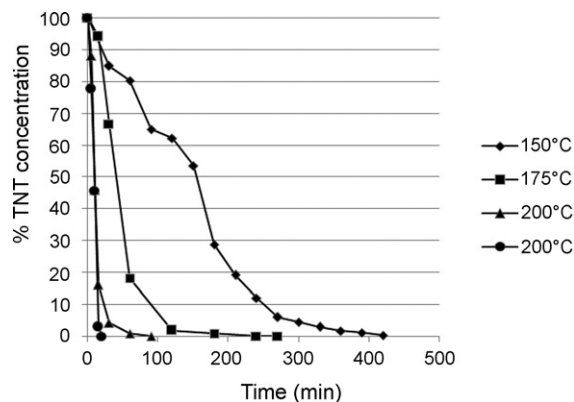


Fig. 2. TNT degradation on contaminated soil at 150, 175, 200 and 225 °C.

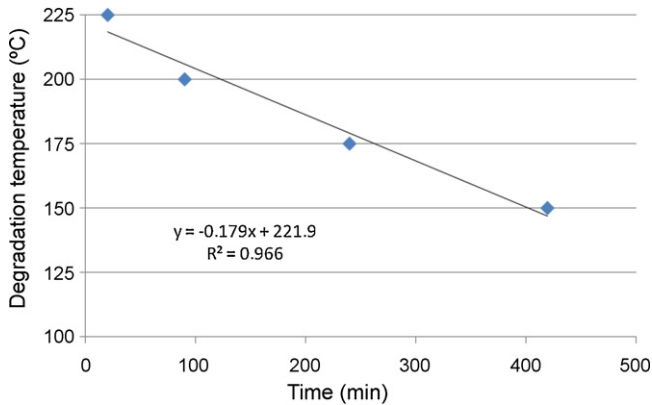


Fig. 3. Plot of the degradation temperatures used in this study against the times required for 100% TNT destruction.

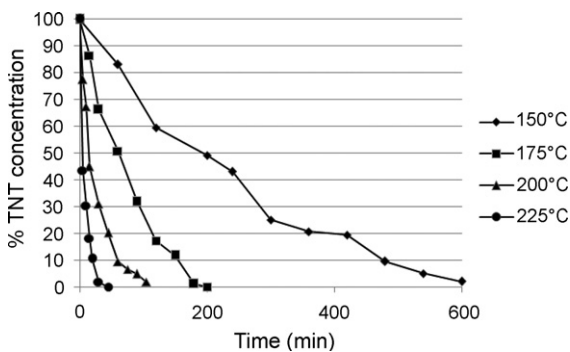


Fig. 4. TNT degradation on sand at 150, 175, 200 and 225 °C.

3.3. TNT degradation spiked on to sand

The degradation of TNT spiked on to sand was examined at the same temperatures as on historically contaminated soil. As shown in Fig. 4, at 150 °C, 97.9% TNT degradation is achieved in 600 min, whereas at 175 °C complete degradation is achieved in 200 min. At 200 and 225 °C, complete degradation is achieved in 120 and 45 min, respectively.

3.4. TNT degradation spiked on to reference soil and in water (no solid matrix present)

The degradation of TNT spiked on to a reference soil and in pure water was examined. This was done to examine whether a solid matrix (soil or sand) affects the degradation rate or not. Fig. 5 shows

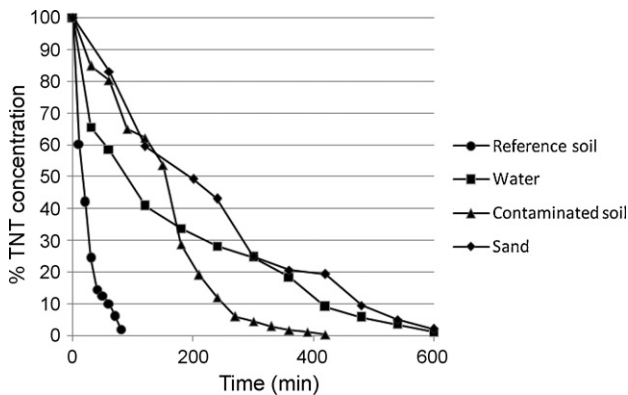


Fig. 5. Comparison of TNT degradation on reference soil, water, contaminated soil and sand at 150 °C.

Table 3

Metals/complexes concentrations in the contaminated and reference soil

Metals/complexes	TNT	Reference soil
Mg	0.44%	0.47%
Al ₂ O ₃	0.90%	0.93%
Fe	1.87%	2.15%
Zn	0.79%	1.08%
Ni	0.453 ppm	0.220 ppm
Cu	0.600 ppm	1.433 ppm

the results of TNT degradation on to reference soil and water. In the case of the reference soil, complete degradation is achieved in 80 min. Approximately 40% of TNT was found in the water phase and 60% in the soil phase after treatment. Since extraction and diffusion of TNT molecules does not occur in this case, this indicates that not all of TNT returned to the soil after cooling but a significant amount remained dissolved in water. In pure water, TNT was 98.8% degraded in 600 min.

3.5. Microanalysis results for metals

The TNT-contaminated soil and the two-reference soil were tested for Mg, Al₂O₃, Fe, Ni, Zn and Cu, to determine whether the concentrations of these substances in the soils affect the rate of TNT degradation. The results are indicated in Table 3.

The concentrations of the metals are very low, therefore it is unlikely that any of the metals acted catalytically in the case of the TNT contaminated soil. However, they may have affected the TNT degradation on the reference soil, since the amount of TNT spiked was only 1000 ppm compared to the much higher amounts of TNT in contaminated soil.

3.6. Comparison of degradation rates on historically contaminated soil, spiked soil and in pure water

Evidence of the processes occurring can be obtained by comparing the rates of degradation of TNT in historically contaminated soil samples, spiked on to soil, sand and simply injected directly in water.

Initially, it is useful to compare the degradation of TNT on sand and in pure water at 150 °C (Fig. 5). As can be seen, the curves and the end-points for the two situations are similar. On sand, 97.9% degradation was achieved in 600 min, compared to 98.8% in water. Therefore, the presence of sand has a minor effect in TNT degradation. It can be concluded that degradation on sand is a good basis for comparisons, when looking for catalytic effects on soils.

We can now compare the degradation of TNT on contaminated soil and sand at all temperatures (Figs. 2 and 4). The times for >99% degradation are comparable to those on the contaminated soil. At 150 °C, it is interesting to see that at the early stages of degradation, the rate is similar. As degradation progresses TNT on soil is degraded a little faster compared to sand. At 175 °C, TNT degradation on contaminated soil progresses more slowly at the beginning compared to degradation on sand (at 15 min, 94 and 86% TNT remains on soil and sand, respectively), however degradation on soil continues at a faster rate and ~99% destruction is achieved in 105 min compared to 180 min on sand.

At 200 °C, in the first 5 min, degradation on soil proceeds more slowly compared to sand. At the end, complete degradation on contaminated soil is achieved in 90 min compared to 120 min on sand. This indicates an increase in degradation rate on soil. At 225 °C a similar trend is observed. In the first 5 min, ~23 and 57% is degraded on soil and sand respectively. However, 100% destruction on contaminated soil is considerably faster than that on sand, 20 and 45 min, respectively. Therefore in all cases, degradation on contam-

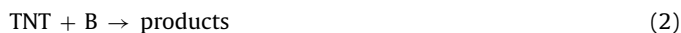
inated soil starts more slowly than on sand, but the rate is increased with time and as a result, complete or near complete degradation on soil is achieved in less time.

There are three possible reasons that one can use to explain the increase in degradation rate: autocatalysis of TNT degradation by a reactive intermediate, slow extraction/diffusion of TNT molecules followed by faster degradation and the exothermicity of the reaction in the case of the historically contaminated soil. These effects are expanded on below.

Autocatalysis is a phenomenon where one or more compounds produced during the reaction, catalyze it. In autocatalysis, the rate of degradation increases, indicating that a substance produced during degradation catalyses the reaction. The slower degradation initially, is followed by a faster rate due to the autocatalytic intermediate(s), ending with a slower degradation as the concentration of the explosive diminishes to zero [34].

In the case of the degradation of TNT, identifying the autocatalytic intermediate(s) may be useful not only from a theoretical but also from a practical point of view. Attempts to analyze the autocatalytic behavior of the system mathematically, were not successful.

The reactions that take place inside the reaction cell are not fully known, therefore there may be more than one autocatalytic intermediate. Additionally, it is likely that concurrent reactions occur, such as



To examine if autocatalysis occurs, the complete degradation pathway has to be determined. This would require identification of all major by-products, their temperature and time of formation and disappearance, which was beyond the scope of this study. However, autocatalysis could occur in both cases of degradation on soil and sand, therefore the differences in degradation cannot be explained through this hypothesis.

The experimental temperature and the heating rate control the time that the degradation products are formed, as well as the duration of their possible catalytic activity. At lower temperatures (150 and 175 °C), processes with lower activation energies and greater exothermicities are favored and there is enough time for stable products to form and serve as catalysts. At higher temperatures (200 and 225 °C), the products have a shorter time to act catalytically [35].

The degradation process may initially governed by a slow, rate-determining extraction step, followed by a rapid degradation step. The initial rate of degradation observed in these graphs could be due to degradation of the TNT molecules located on or near the soil surface. For these molecules extraction does not occur. While this happens, the bulk of TNT that exists in the core of the soil particles, is being extracted and for them extraction is the rate-limiting step before the reach the soil surface and degrade. As soon as they reach the soil–water interface, they degrade and this is indicated by the faster-rate observed in the graphs.

Finally, in the degradation of TNT on contaminated soil the change in degradation rate may also be due to self-heating of the system. This self-heating is a result of the exothermic reactions that occur during degradation. The heat generated is significant since the TNT concentration on the contaminated soil was 120,000 ppm. One also has to take into account the nature of TNT present in the contaminated soil and that spiked on the reference soil. The former is rather crude with impurities and has undergone several processes (e.g. weather effects, soil aging, open burn/open

detonation), whereas the latter are in pure, unprocessed form. Mak-simov [38] has proposed that impurities sharply change the rate of decomposition of nitroaromatic compounds. Furthermore, the TNT concentration on the contaminated soil is ~120,000 ppm, compared to the 1000 ppm on the reference soil and sand.

We have to assume that the heat produced during degradation is the heat of TNT detonation, which is 4476 kJ/kg. The amount of TNT present in 1 g of soil will give, when detonated, 537 J of energy. Since we already know the specific heat capacity of water [33], soil [36] and stainless steel [37], the temperature increase of the system can be calculated. Therefore, the 537 J produced, will increase the temperature of the system by 8.7 K. This temperature increase is substantial considering the rule of thumb that the rate of a reaction increases twofold every 10 K. However, one has to remember that some of the heat generated by the TNT reactions will be lost. All three effects may be important in some cases.

By comparison of the TNT degradation on the contaminated and reference soil at 150 °C (Fig. 5), TNT degrades much faster on the reference soil, 80 min compared to 420 min. Provided that the two soils show no major structural or other differences, the slower degradation on contaminated soil can be appointed to the time required for the TNT molecules to be extracted and diffused from the soil matrix to the water phase. This mass transfer limitation is not present in the case of the reference soil.

If we compare the degradation rates of TNT spiked on to sand and reference soil at 150 °C (Fig. 5), it is obvious that degradation on the reference soil, proceeds much faster. Complete degradation on spiked soil is achieved in 80 min compared to >600 min on sand. In both cases, the amounts spiked are the same and the extraction/diffusion step does not occur, therefore the reason for the faster degradation on the reference soil is the catalytic effects of the soil surface or any substances that exist in the soil. The levels spiked on to soil are quite low (1000 ppm) and small amounts of organics and other reagents in the soil can have a large effect. Several studies reviewed by Brill and James, showed that many compounds, including essentially any source of H⁺, accelerate the rate of TNT decomposition [35]. One or more of such organic compounds may be present in the reference soil.

4. Conclusions

Although much work has been done in the degradation of TNT under oxidative conditions (e.g. wet air oxidation), no data are available on the interactions of TNT on aged contaminated soil with subcritical water under non-oxidative conditions. The presence of soil, largely increases the complexity of the system, therefore more research is required to clarify the exact degradation pathway and all the by-products that are formed. Our results have shown that effective remediation of TNT-contaminated soil can be performed at a range of temperatures, starting as low as 150 °C. There is a mass transfer limitation in the degradation of TNT on aged, contaminated soils, which controls the rate of degradation. Additionally, the soil matrix or any organic substances that exist in it act catalytically to some extent. Finally, no clear evidence was found that self-heating or autocatalytic effects are taking place.

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