EXPERIENCE WITH TREATMENT ALTERNATIVES FOR ORGANOHALOGEN CONTAMINATION

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Through several years of research, development, and demonstration testing and evaluation of environmental contamination problems, experience and expertise in treatment technologies have been accumulated that are specific and relevant to organohalogen contamination. Contamination situations include soils, sludges, fluids, and surfaces. This paper will summarize that experience and some of the conclusions that have been drawn.

1.0 INCINERATION: A Hybrid Thermal Treatment System (HTTS) has been commercialized that is a direct fired, countercurrent rotary kiln with a secondary combustion chamber and a flue gas cleansing system that stack testing has shown exceeds regulatory requirements. The patented design of this thermal destruction process incorporates both pyrolytic and oxidative conditions in the kiln to optimize combustion, ash burn out, and auxiliary fuel requirements. The first three HTTS units have been built for maximum feed flexibility and have thermal capacities of 40 - 60 million BTU per hour. A downsized HTTS has been built for the Italian market and a third "super kiln" is under construction for very large soil decontamination projects.

HTTS-1 has decontaminated 140,000 tons of soil contaminated with TNT at rates of 10 - 20 tons per hour.[1] HTTS-2 and 3 are in start-up on a site to treat oils, sludges, and soils.

Important factors in cost-effective performance that have been learned from these operational experiences are: 1) proper feed preparation and handling, 2) provisions for coping with slag buildup, 3) system reliability, and 4) throughput. As a result of emphasis on optimizing these factors, the cost of incineration has come down dramatically in recent years to under $200 per ton for large jobs.

2.0 LOW TEMPERATURE THERMAL SEPARATION: This technology differs from incineration in that indirect heating of the solids or sludges is used to volatilize organics to decontaminate the resultant treated soils. This results in a significantly less gas volume leaving the thermal separator and consequently smaller downstream equipment. When the volatilized contaminants are condensed and collected as a concentrate for treatment, this technology is a physical-chemical treatment process. Extensive pilot-scale (20 - 50 kg/hr) testing of this thermal separation/condensation technology has been conducted on dioxin, PCB, and PAH-contaminated soils. Desorption temperatures tested ranged from 300 C to 550 C and residence times ranged from 4.3 to 45 minutes.

Dioxin (TCDD) on two soils at 200 - 500 ppb was reduced to <1 ppb, collected in an organic solvent, and destroyed by ultraviolet (UV) photolysis.[2,3] Five different PCB-contaminated soils (35 to 44,000 ppm) were treated to <2 ppm PCBs.[4] On two of the soils, the thermal separation treatment tests were used to show the effectiveness of the technology in separating PCBs from soils that were also contaminated with uranium and technetium. Three soils contaminated with PAHs were treated to <1 ppm after 8 minutes at 400 C.

Other important results and observations from these pilot tests are: 1) Proper feed preparation and handling are required; 2) Higher concentrations of PCBs (e.g. 4.4%) require higher temperature to achieve decontamination goals; 3) Trace levels of PCDFs form during PCB treatment, and high treatment temperatures >500 C are required to drive them off the soil; 4) Depending on the quench liquid used in the condensation of volatilized materials, the number of phases in the condensate can range from two to four, with attendant processing difficulties proportional to the number of phases; 5) Condensed organohalogen contaminants can be destroyed on-site by one of two treatment methods -- UV photolysis or alkali metal polyglycoxide dehalogenation (e.g. KPEG).

3.0 UV PHOTOLYSIS: R&D on other treatment technologies for soils contaminated with organohalogens has shown the ability of direct surface UV photolysis of TCDD- and PCB-contaminated soils to be effective when the soil surface is sprayed with a surfactant solution.[5] Irradiation of contaminated soils with a medium pressure mercury arc lamp, with periodic tilling of the soil and surfactant spraying, has reduced TCDD from 671 ppb to 11 ppb in 31 hours. PCB contamination on soil was reduced from 725 ppm to <0.5 ppm in 15.5 hours. The effectiveness of this treatment technology will be demonstrated on a pilot scale under a 2 year cooperative agreement with the U.S. EPA in the SITE Emerging Technologies Program.

4.0 DIRECT KPEG TREATMENT OF SOIL: In a project funded by the U.S. Navy and EPA, pilot-scale tests were conducted on of the use of KPEG reagent, directly applied to soil, to destroy PCBs.[6] Soil and KPEG reagent are combined in a mixer, heated to 140 C to remove moisture and cooked for 4 hours to carry out the dehalogenation reaction. Spent reagent and by-products were left on the soil. Nine batches of soil, 1500 kg each, were treated to <2 ppm PCBs. Important observations from these pilot tests are: 1) Washing of the soil with water to remove spent reagent was difficult to achieve, and 2) The amount of reagent required in these tests resulted in very high reagent costs, but new R&D by the U.S. EPA indicates that significant reductions in the amount of reagent required can be made.

5.0 REAGENT TREATMENT OF OILS: A variety of chemical dechlorination reagents have been patented and tested for treatment of waste oils contaminated with aromatic organohalogens. IT has had direct pilot experience with two reagents -- the Niagara-Mohawk modified KPEG system and the Sea Marconi (Italy) solid reagent. The former is a mixture of KOH, polyglycols, and dimethyl sulfoxide (DMSO). The latter is a blend of an alkali metal alcoholate and a polyethylene glycol on a solid, inert substrate. All reagents involve phase transfer chemistry.

U.S. KPEG reagents are liquids/slurries and are reacted with contaminated oils in heated batch reactors at 100 C - 150 C. After the dechlorination reaction, the treated oil is decanted from the reagent. Depending on the oil being treated and the organohalogens concentration, the reagent may be used to treat more than one batch of oil.

The Niagara-Mohawk reagent and trailer mounted commercial treatment system was used to treat 64,000 liters of dioxin-contaminated oils at Butte, MT, and Kent, WA.[7] The reagent was successful in destroying dioxins and furans to nondetectable levels. Initial concentrations of the various PCDDs and PCDFs ranged from 120 ppb to 200 ppm.

It was also used to successfully treat 18,000 liters of PCB-contaminated transformer oils to reduce PCBs from 1000 ppm to <2 ppm.

Pilot tests have shown the ability of the Sea Marconi solid reagent to treat transformer oil contaminated with 1800 ppm *Arochlors*. The contaminated *oil* was circulated through one kg of reagent for 90 hours at 80 C at which time the Arochlor 1200 concentration was <10 ppm. Trichlorobenzene was also reduced to <100 ppm.

Key factors in the commercial success of the use of these chemical reagents to decontaminate fluids are: 1) the availability and cost of incineration for the organohalogen-contaminated fluid, 2) concentration of organohalogen in fluid, 3) availability and cost of disposal of spent reagent, and 4) reuse options for decontaminated oil.

6.0 REAGENT DECONTAMINATION OF SURFACES: Field evaluations have been conducted on the use of the Sea Marconi reagent in liquid form to decontaminate surfaces contaminated with PCBs and dioxins. One successful test involved three successive applications of hot reagent to a concrete floor. After 2 weeks core samples were taken and the reduction in PCB concentration in the top 0.64 cm of concrete ranged from 11 to 97%, with an average of 73% (range was 0.64 to 6.22 mg/kg). These results show penetration of the reagent into the concrete. In another PCB-contaminated concrete test, the test conditions were less favorable. The floor was cold and covered with carbon black as well as the PCBs. Initial PCB contamination ranged from 100 to 2300 g per 100 cm2. Wipe samples were used to evaluate effectiveness. Reductions of 50% were shown after each of two successive reagent applications 24 hours apart.

Important factors in the ability of a liquid chemical reagent to treat contaminated surfaces are: 1) the ambient conditions, 2) cleanliness/porosity of the concrete, 3) depth of contamination, 4) treatment goals, 5) future use of the area, 6) treatment time, and 7) cleanup and disposal of the reagent.

This technology has as its chief advantage compared to other surface decontamination technologies that it destroys the PCBs.

7.0 CONCLUSION: These technologies are representative of the various technological alternatives to dealing with organohalogen-contamination. Other techniques that continue to be evaluated experimentally and in engineering studies include stabilization, biodegradation, catalytic reduction, and plasma destruction.

These experiences in development and commercialization of new and innovative technologies have taught that the selection of the optimum treatment system in performance and cost involves several factors: 1) treatment criteria, 2) concentration of contaminants, 3) presence of other contaminants, 4) matrix to be treated, 5) disposal of treatment residuals, 6) availability and cost of other alternatives, 7) permitting and regulatory approvals, and 8) acceptability to the public.

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