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The Clean-Up Begins

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The handling of dioxin-contaminated soil has become an important issue here in Missouri cropping up when when Times Beach became contaminated and, before that, Minker-Stout. The Minker-Stout area seemed to be somewhat manageable, because it was much smaller, but when we had to consider dealing with 800 acres contaminated with 100 parts per billion of this particular material, the volume of dirt to be dealt with became much more significant and the alternatives for clean up narrowed. The critical thing from an environmental standpoint is that 2,3,7,8-TCDD is an extremely stable compound and, for that reason, the destruction and management of this compound becomes a problem. If any one of the chlorine rings is removed, whatever compound results is much less stable and subsequently a natural degradation process can start to take place, or a thermal or chemical process can act with this chemical to destroy it.

An important consideration in dealing with dioxin is some of its chemical properties (Table 1). It has a melting point of about 302°C

Table 1. Properties of dioxin (2,3,7,8) important to behavior in soil

MP	302-305°
Vapor Pressure (mmHg)	10^{-6}-10^{-7}
Water Solubility (ug/L)	0.2
Partition Coefficient	
Octanol/Water	13,800,000
Soil/Water	23,000
Biota/Water	110,000
Solubility (mg/L)	
Benzene	570
MeOH	10
Acetone	110
Chloroform	370
O-dichlorobenzene	1,400

and reaches combustion about 2200° F. It has a very low vapor pressure of 10^{-6}-10^{-7} millimeters of mercury, meaning that it tends not to evaporate. It is extremely insoluble in water; that is, 200 parts per trillion solubility with pure material. This would indicate we have a fairly stable compound. Wherever dioxin contamination exists, especially in soil, it tends to remain in place. In order to look at dioxin contaminated dirt, we took some of the samples from the Minker site which contained 400 parts per billion and tried to extract that with water. We found it was non-detectable at 1 part per trillion.

The problems that we face in cleaning up dioxin contamination are: What will happen to this material? Is it going to leak anywhere? Is it going to contaminate somebody else after you finish managing it? Data indicate that dioxin is extremely stable and it is even more stable on soil. The movement of the material through the environment would not be likely to occur if soil erosion could be controlled.

The Governor of Missouri identified a Task Force to look at all alternatives for a solution. The Governor's Task Force was an unbiased professional body who looked at various options that were presented to them for destruction of dioxin. There are a variety of options which are fairly straightforward; the soil can be left in place and the place can be secured, or the soil can be removed and consolidated at some other site or treated.

Once the soil is removed from the site, a variety of technical options become available (Table 2). One option is interim storage piles for feeding to a facility for size reduction. An incinerator or a solvent extraction process can be used, and the solvent can be concentrated and degraded through a chemical or ultraviolet process. Interim storage might be needed while some special type of technology is developed to take care of the problem. All of these processes require securing the dirt on-site or off-site, about 500,000 cubic yards of dirt, an extremely large quantity of material. Any of these processes, incineration or solvent extraction, basically are intended to remove a very low concentration of dioxin. After the process is complete, nearly the same amount of dirt remains, and, under federal law, must be dealt with as a hazardous waste.

The Task Force looked at all of these options. Through their eight month tenure, they heard from experts from all over the world, and they came up with a specific recommendation to the Department. The technical processes for destroying dioxin which we considered were: radiation treatment, gamma radiation, chemical treatment, dechlorination, ruthenium tetroxide, chloridized ozone, chemical dechlorination, layer oxidation and molten salt combustion. All of these are pilot processes. Some of these, like ozone, ultraviolet light and chemical dechlorination have worked in solvent phases. Many of them have worked on pure dioxin in solvent phases.

The critical thing that the task force found after hearing the options available was that no one has ever burned dioxin-contaminated

Table 2. Technical options for degradation of dioxin.

Process/Technology	Description	Byproducts	Commercial Status
RADIATION TREATMENT			
UV degradation	TCDD is irradiated with sunlight or high pressure mercury lamps in the presence of a suitable hydrogen donor after solvent extraction from soil. TCDD in solvent is irradiated with gamma radiation	Solvent with TCDD decomposition products	Commercially done at Verona
Gamma	TCDD in solvent is irradiated with gamma radiation	Solvent with TCDD decomposition products	Laboratory tests on TCDD in solvent
CHEMICAL TREATMENT			
Catalytic dechlorination	TCDD in solvent is dechlorinated with Nickel Borohydride catalyst	Solvent with TCDD decomposition products	Conceptual
Chlorination	TCDD in solvent is extensively chlorinated between 600° and 800° psig	Solvent with TCDD decomposition products of CCl_4, HCL, and $COCl_2$	Piloted on herbicide orange
Ruthenium tetroxide	TCDD in solvent is oxidized with ruthenium tetroxide	Solvent with TCDD decomposition products	Laboratory tests only
Chloroiodides	TCDD is reacted with chloroiodides in a micellar solution	Solvent with TCDD decomposition products	Laboratory tests only
Ozone/UV	TCDD in solvent is reacted with ozone and irradiated with ultraviolet light	Solvent with TCDD decomposition products	Laboratory tests only
Chemical dechlorination	TCDD is reacted with an aromatic liquid and alkaline reactants	Solvent with TCDD decomposition products	Laboratory tests only
THERMAL TREATMENT			
Wet air oxidation	TCDD is catalytically oxidized at 200° C in a wet air oxidation process	TCDD decomposition products	Laboratory tests with TCDD
Conventional hazardous waste incineration	TCDD in soil or solvent is combusted in a hazardous waste incinerator	TCDD decomposition products	Commercial incineration available for PCBs, other hazardous wastes; TCDD incinerated with herbicide orange on the M/T Vulcanus
Molten salt combustion	TCDD in solvent is injected below the surface of a molten salt bath in a reactor at 1500° F to 1800° F	TCDD decomposition products; spent molten salt melt	Laboratory tests with chlorinated hydrocarbons
Microwave-plasma destruction	TCDD in soil or solvent is mixed with partially ionized gas produced by microwave-induced electron reactions	TCDD decomposition products	Pilot-scale tested on PCBs and other toxic products/materials
Pyrolysis	TCDD in soil or solvent is decomposed by heat alone	TCDD decomposition products	Conceptual

dirt before and been able to show that dioxin was actually destroyed. The current techniques for monitoring air pollution from incinerators do not indicate whether the dioxin has merely been evaporated from the soil or actually destroyed, because the concentrations are so low that those levels cannot be measured with today's stack testing technology. When we looked at all of these options, we were convinced that the technology is around the corner but the problem is here now with people living on the dirt. Table 3 shows an outline of an indication of the proposed cost of incineration during December of 1983. These estimates are just for very few sites -- the Minker site, Stout site, Romaine Creek, Shenandoah stables, Bubbling Springs Stables and Timberline Stables. The estimates of volume of contaminated soil totaled about 131,000 cubic yards for these six sites. Using incineration technology that was available last December-January, burning this dirt at the EPA mobile incinerator would have taken 31 years to accomplish at a cost of $113 million. That would not even start to deal with Times Beach. We figure there is about 300,000 cubic yards of contaminated soil at Times Beach alone.

Table 3. Mobile Incinerator at Missouri Sites

Site	Size (ft)	Approximate yds.	Cost ($)	(year)
Minker	300 x 300 x 10	33,333	20,833,000	5.7
Stout	200 x 150 x 20	22,222	13,889,000	3.8
Romaine Creek	100 x 6000 x 5	111,111	69,444,000	19.0
Shenandoah	100 x 300 x 10	11,111	6,944,000	1.9
Bubbling Spring	100 x 100 x 5	1,852	1,158,000	0.3
Timberline	100 x 100 x 5	1,852	1,158,000	0.3
Times Beach	NA			
Verona	NA			
Denny Farm	NA			
		181,418	113,426,000	31.0

Even if the maximum capacity of the incinerator could be used the time requirement would be 7.0 years just for these sites. The cost at the greater feed rate would be $25,206,000.

Subsequently, we did have an opportunity to go to Texas and look at the Rollins incinerator, which is the only incinerator in the country approved to burn PCBs. PCBs have a chemical constituency configuration similar to dioxin, namely biphenyl rings with chlorines on it and are likewise a very tough material to burn. Rollins has had experience with burning PCB contaminated dirt, and they would only guarantee 97% destruction of the contamination. So, if we start out with soil contaminated at 100 parts per billion, we could end up with contamination of only three parts per billion, and we would still have dioxin-contaminated dirt. While taking care of 97% of the problem, the remaining soil would still not meet health standards for residential areas.

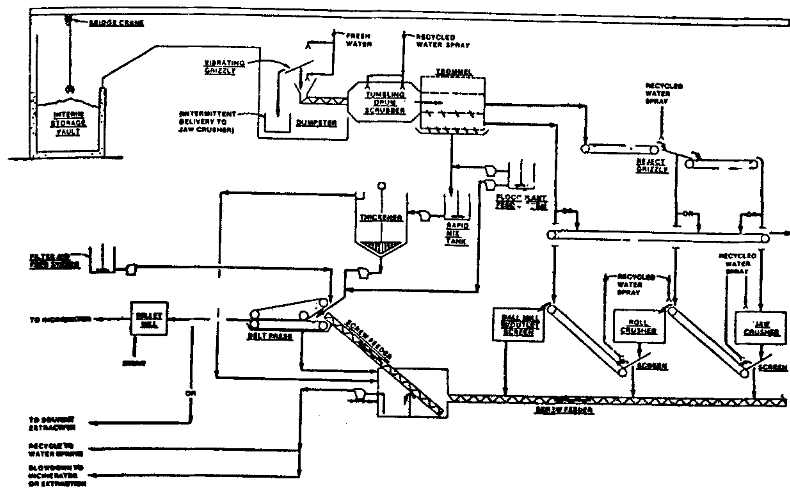

Figure 1. Size reduction conceptual flow diagram.

Another problem in managing dirt is that, if it is going to be fed to an incinerator or a solvent extraction plant, it must go through a size reduction process (Figure 1). For a size reduction process, interim storage is necessary. There is a similar process which is currently used in making cement, and, if you have ever been in a cement plant, you know that the process is extremely dusty. A potential exposure exists for workers around such a facility with a potential associated risk which has to be balanced against other management risks.

In order to incincerate dioxin, the dirt must be heated to about 1600° F, which vaporizes the dioxin (Figure 2). The dioxin gasses then go into the afterburner at 2300° F, the temperature currently thought necessary to destroy dioxin gasses in about two seconds residence time. The gas then goes through air pollution equipment to insure that no contamination goes up the stack. As mentioned earlier, there are some technological limiting factors for determining what can be measured going out that stack. A very small quantity of dioxin is being added to a large volume of air, and when the dioxin is diluted that much, the detection limit becomes very critical for showing that 99.9% of the contamination was destroyed.

In a solvent extraction process, once the soil has been crushed and sized so there will be good contact between the solvent and the soil, the soil can be put into the solvent washers. Solvent is run through the water and the dirty solvent comes out the back and then is sent

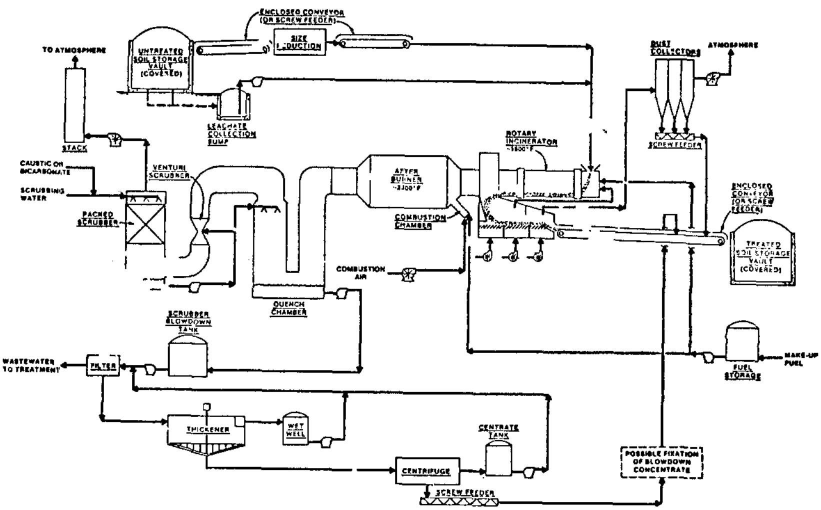

Figure 2. Incineration of dioxin-contaminated soil. Conceptual flow diagram.

to a solid reclamation process, which is basically an evaporator. The solvent is evaporated off and the dioxin comes out the bottom. One company proposed a reagent to destroy the dioxin. In this particular process we would be taking a relatively low concentrated soil and making a relatively highly concentrated dioxin material so that instead of dealing with 100 parts per billion dioxin, we would have to deal with material that contains high percentages of dioxin in a readily availble form absorbable through the skin.

After hearing all of this positive testimony on how to deal with dioxin, the Missouri Dioxin Task Force came up with some basic recommendations. The final Task Force report recommends that a central storage facility be identified for Missouri's dioxin contaminated soil until proven technology is available to deal with the problem. The Task Force came to the conclusion that there is no current proven technology to deal with dioxin contaminated dirt and that we should at least secure the material at one location so that the public is prevented from coming into contact with the dioxin. We also recom mend that the facility be built where that material does not have an opportunity to contaminate the environment and bioaccumulate (Figure 3). The Task Force also recommended that health studies on Missouri citizens potentially exposed to dioxin be done to assess the long-term public health.

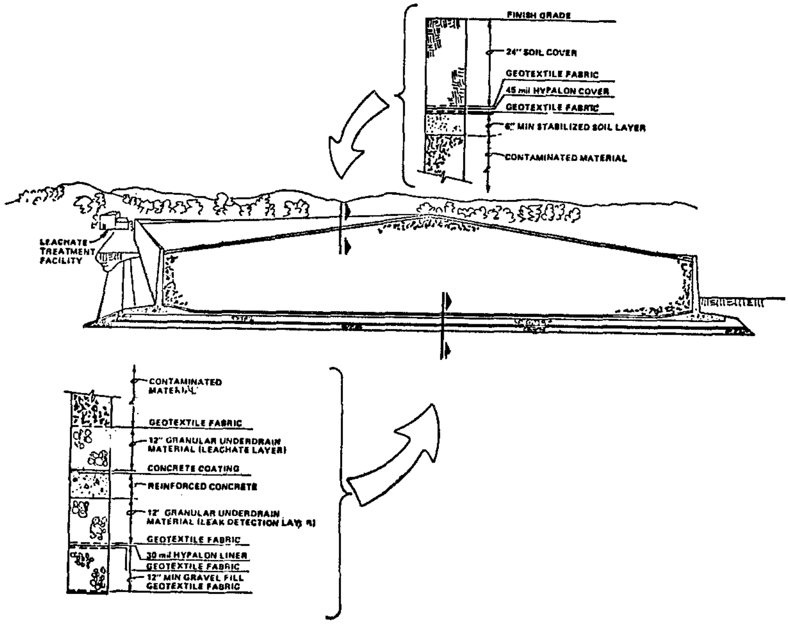

Figure 3. Conceptual design. Concrete takn with flexible cover.

The Task Force also recommended development of a specific strategy for designing/securing a central storage facility. Basically, the Task Force was not happy that the four agencies, DNR, EPA, CDC, and Missouri Division of Health, had not identified a unified strategy for dealing with the problem that a citizen could look at and understand which way govenment was going. We felt that area was particularly important, so that all of the dioxin sites, regardless of whether or not they meet EPA Superfund criteria, could be handled uniformly. The central storage facility should be used only for dioxin contaminated soil. The Task Force felt that we needed to deal only with dioxin contaminated soil and not deal with other hazardous wastes, such as other solvent contaminated dirt, that potentially could cause migration of dioxin contaminated soil. Dioxin contaminated soil without other solvents, in our opinion, is relatively stable and a facility can be designed much more securely.

The Task Force also placed a high priority on the development of expedited schedules for sampling and analysis. Sampling and analysis is a critical problem in trying to deal with these particular sites. Sampling procedures which take six weeks to two months before data come back to determine degree of contamination are not acceptable from a clean up standpoint. The central storage facility should be used only for dioxin contaminated soil. The Task Force felt that we needed to deal only with dioxin contaminated soil and not deal with other hazardous wastes, such as other solvent contaminated dirt, that potentially could cause migration of dioxin contaminated soil. Dioxin contaminated soil without other solvents, in our opinion, is relatively stable and a facility can be designed much more securely.

The primary aim should be reconstruction and reinhabitation of all sites. The Task Force felt that clean up was more appropriate than buy out; therefore our plan should be the reconstruction, clean up and removal of the problem so we can definitively deal with it later.

The state should establish a uniform policy regarding residents. The citizens have not had a good program put before them so they can understand how they will be treated, and the Task Force felt that the criteria and uniform policy regarding sites would be appropriate. They also recommended that we seriously look at the experience gained by the Italians at Seveso after their seven years of dealing with the problem. They recommended that the residual level of dioxin allowed to remain after excavation be specified. The CDC and Division of Health will need to determine the acceptable levels, namely what level people can be expected to live with after clean up is completed, realizing that a zero concentration can never be achieved with current technology or available funds.

The state should begin immediately to communicate the criteria for safe transportation of dirt. The Task Force felt that safe transportation is available through our basic technique for handling contaminated material, but the public needs to be aware of that. A program on toxicology should be established so that we can adequately deal with this problem in the future, and an advisory panel should be set up.

The Task Force's report was delivered to the Governor and the EPA on November 1, 1983, on schedule. Subsequently, the EPA agreed to do an independent analysis, as required by federal law. The outcome of that analysis provides several options: stabilization in place, interim storage on-site, disposal of soil off-site, incineration, solvent extraction or interim storage off-site. In order to stabilize dirt in place at these six sites, the approximate cost is $41 million; interim storage on-site, for six separate sites -- $35 million; disposal off-site -- $32 million; incinceration using current technology -- $111 million; solvent extraction -- $151 million; and interim storage at a central storage facility -- $15.8 million. For any of these various options, the issue of insurance arises when moving large quantities of dirt. Possible air emissions, surface and groundwater contamination, and soil contamination must be considered. Each of these processes must be addressed so that work does not recontaminate the area being cleaned up, create dust going beyond the property line or cause the level to be in excess of one part per billion. Material removed from the site must be transported so that it does not contaminate the road.

The Governor's Task Force has recommended that Times Beach be identified as a potential storage site. The State concurs with that recommendation. The EPA has evaluated alternative sites, and they also have concurred with that recommendation. The six sites being considered for clean-up are: the Minker site, the Stout site, Cashel and Jones (which are two small contaminated areas), Castlewood (where there are currently people living on the area that is contaminated along the streets), Quail Run Mobile Home Park and Piazza Road. We are hoping to begin the clean up of those six sites by July 1, 1984. Design of a much larger facility would start about July 1, 1985 with the start of construction about two years from now and completion of clean up about five years from now. The EPA is studying this proposal and we are expecting them to come up with a feasibility study on the larger facility by June of next year. The feasibility study on this smaller facility is out and calls for building a two acre storage facility.

There are different ways to deal with the flood plain issue. You can raise the facility above flood elevation, it can be diked or it can be built to withstand a 100 year flood. A concrete tank with a flexible cover is currently being proposed for the Times Beach area. This facility is designed to hold 50,000 cubic yards, to withstand a 100 year flood and to contain the material until a larger facility can be built to handle all of the material or until technology can be identified to solve the problem.

It is our goal to have the public hearing soon, a decision made by EPA the end of December, 1983 and the appropriate permits and variances by April, 1984. Site preparation could start April and we could begin moving dirt and cleaning up the six sites in July of 1984. To give you some idea of the variety of federal agencies and state agencies involved and how we are trying to coordinate this effort: we have FEMA involved because of the flood plain; we have local government involved because of public participation; design and construction contractors are designing the facility; the public is involved in commentaries throughout this whole process; Army Corps of Engineers deals with the flooding, levying and answering any questions pertaining to the impact of a facility at Times Beach on floods upstream or downstream; and DNR is involved in the permitting, overseeing and review of the design, along with EPA. That does not even address the health questions that are going to come up throughout the process.