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SUPERFUND INNOVATIVE TECHNOLOGY EVALUATION

Emerging Technology Summary

Babcock & Wilcox Cyclone Vitrification

The Babcock & Wilcox 6 million Btu/hr pilot cyclone furnace was successfully used in a 2-yr Superfund Innovative Technology Evaluation (SITE) Emerging Technology project to melt and vitrify an EPA Synthetic Soil Matrix (SSM) spiked with 7,000 ppm lead, 1,000 ppm cadmium, and 1,500 ppm chromium. An advantage of vitrification over other thermal treatment technologies is that in addition to destruction of organic wastes, the resulting vitrified product captures and does not leach non-volatile heavy metals. Indeed, when operated at 50 to 150 lb/hr of dry SSM feed, and from 100 to 300 lb/hr of wet SSM feed, the cyclone technology was able to produce a non-leachable product (as measured by TCLP) from the hazardous soil. From 95% to 97% of the dry input SSM was incorporated within the slag. Stable cyclone operation was achieved during the 2-yr project which processed over 6 tons of clean, unspiked SSM and 5 tons of spiked SSM. During the thermal vitrification process, the heavy metals partition between the vitrified slag and the stack flyash. The capture of heavy metals in the slag was found to increase with increasing feed rate and with decreasing metal volatility. The treatment of the synthetic soil matrix resulted in a volume reduction of 25% to 35% (dry basis). Vitrification results in an easily-crushed, glassy product.

This summary was developed by EPA's Risk Reduction Engineering Laboratory, Cincinnati, OH, to announce key findings of the SITE Emerging Technology program that is documented in a separate report (see ordering information at back).

Introduction

Organization of this Project Summary

The Babcock & Wilcox (B&W) cyclone vitrification process has been developed and tested for treatment of a U.S. EPA-developed Synthetic Soil Matrix (SSM) contaminated with heavy metals. This technology is significant because it combines incineration with the production of a non-leachable (heavy metals and radionuclides) soil residue. Organics are combusted and destroyed in the cyclone furnace while melting the soil to form a vitrified slag. Non-volatile metals (e.g., chromium) and non-volatile radionuclides (e.g., strontium and zirconium) partition mainly to the vitrified slag where they are rendered non-leachable. The process description, operation, and applicable wastes are discussed in the sections below.

In this Summary, results from two separate cyclone vitrification projects occurring between 1990-1992 are discussed. The projects (Phases I and II) were sponsored under the U.S. EPA SITE Emerging Technologies Program. Both projects were performed on the B&W 6 million Btu/hr pilot cyclone test facility. Brief descriptions of the two projects are given below:

- **Phase I Emerging Technologies Project** - In this project, a dry synthetic soil matrix spiked with lead, cadmium, and chromium was vitrified to determine cyclone furnace operation conditions (process feasibility), heavy metals leachability in the vitrified slag, volume reduction, and preliminary heavy metals mass balance (i.e., how much of each metal was retained in the vitrified slag and how much volatilized).
- **Phase II Emerging Technologies Project** - Once feasibility was established in Phase I, a wet feed system was constructed and furnace modifications performed to optimize the throughput of soil and increase heavy metals capture in the slag. Wet SSM (wet soil is often encountered at Superfund sites) spiked with lead, cadmium, and chromium was vitrified to determine heavy metals leachability, volume reduction, and detailed heavy metals mass balance.

On the basis of the results of Phases I and II, Babcock & Wilcox was asked to perform a SITE Demonstration. The Demonstration results may be obtained from the EPA Project Officer.

Technology Development at Babcock & Wilcox

The Babcock & Wilcox cyclone furnace is a well-established design (over 26,000 MWe installed electrical capacity) for the combustion of high inorganic content (high ash) coal. The combination of high heat release rates (450,000 Btu/cu ft for coal) and high turbulence in cyclones assures the high temperatures required for melting the high-ash fuels. The inert ash exits the cyclone furnace as a vitrified slag.

Taking advantage of the ability of the cyclone furnace to form a vitrified slag from waste inorganics, the cyclone furnace was used in a research and development project to vitrify municipal solid waste (MSW) ash containing heavy metals. The cyclone furnace produced a vitrified MSW ash which was below EPA leachability limits for all eight RCRA metals. The successful treatment of MSW ash suggested that the cyclone vitrification technology would be applicable to high inorganic content hazardous wastes and contaminated soils that also contain organic constituents. These types of materials exist at many Superfund sites, as well as sites where petrochemical and chemical sludges have been disposed. Our approach for establishing the suitability of the cyclone vitrification technology relies on the premise that for acceptable performance in treating contaminated soils containing organic and heavy metal/radionuclide constituents, the cyclone furnace must melt the soil matrix while producing a non-leachable slag and must achieve the destruction and removal efficiencies (DRE's, currently 99.99%) for organic contaminants normally required for RCRA hazardous waste incinerators. The high temperature (>2,500 to 3,000 °F), turbulence, and residence time in the cyclone and main furnace are expected to result in high organics destruction and removal efficiencies (DRE's).

Process Description

The Babcock & Wilcox 6 million Btu/hr cyclone furnace located in Alliance, OH, was used to perform all pilot-scale vitrification tests. The furnace is water-cooled and simulates the geometry of B&W's single cyclone, front-wall fired cyclone coal-fired boilers. This cyclone facility has been proven to simulate typical full-scale cyclone units in regard to furnace/convection gas temperature profiles and residence times, NO_x levels, cyclone slagging potential, ash retention in the slag, unburned carbon, and flyash particle size. It is important to note that this particular furnace configuration, representative of a fossil fuel-fired utility boiler, is likely to be modified significantly for a transportable unit dedicated to soil vitrification.

The pilot cyclone furnace, shown in Figure 1, is a scaled-down version of a commercial coal-fired cyclone with a restricted exit (throat). The furnace geometry is a horizontal cylinder (barrel). A schematic of the process is illustrated in Figure 2. For the present application, natural gas and preheated combustion air (820°F) enter tangentially into the cyclone burner. In dry soil processing, the soil matrix and natural gas enter tangentially along the cyclone furnace barrel. For wet soil processing, an atomizer using compressed air is used to spray the soil paste directly into the furnace. The soil is captured and melted, and organics are destroyed in the gas phase or in the molten slag layer formed and retained on the furnace barrel wall by centrifugal action. The soil melts, exits the cyclone furnace from the tap at the cyclone throat, and is dropped into a water-filled slag tank where it solidifies. A small quantity of soil also exits as flyash with the flue gas from the furnace and is collected in a baghouse. In principle, this flyash could be recycled to the furnace as indicated in Figure 2 to increase the capture of metals and to minimize the volume of the potentially hazardous waste stream.

The energy requirements for vitrification were 15,000 Btu/lb. Given the much larger surface-to-volume ratio of the relatively small pilot unit and its cool surface, one may expect a full-scale unit to achieve lower energy requirements.

Particulate control is achieved by way of a baghouse. To maximize the capture of metals, a heat exchanger is used to cool the stack gases to approximately 200°F before entering the baghouse. Although the cyclone facility is equipped with an acid gas scrubber, it was not used for these tests because acid gas generation (e.g., HCl) from the vitrification of the U.S. EPA SSM was expected to be low.

Applicable Wastes and Soils and Possible Technology Configurations

An advantage of vitrification over other thermal destruction processes is that in addition to the destruction of organic constituents, the resulting vitrified product captures and does not leach non-volatile heavy metals or radionuclides. The cyclone vitrification technology would be applicable to high inorganic content hazardous wastes, sludges, and contaminated soils that contain heavy metals and organic constituents. The wastes may be in the form of solids, a soil slurry (wet soil), or liquids. To be treated in the cyclone furnace, the ash or solid matrix must melt and flow at cyclone furnace temperatures (2400 to 3000 °F). Because of the technology's ability to capture heavy metals in the slag and render these non-leachable, an important application of the technology is contaminated soils which contain non-volatile radionuclides (e.g., strontium, transuranics).

The cyclone furnace can be operated with gas, oil, or coal as the supplemental fuel. The waste may also supply a significant portion of the required heat input. Additional air pollution control devices, such as NO_x reduction technologies, can be applied as needed. An acid gas scrubber would be required, for example, when chlorinated wastes are treated. HEPA/carbon/scrubbing towers would be used for radioactive waste processing.

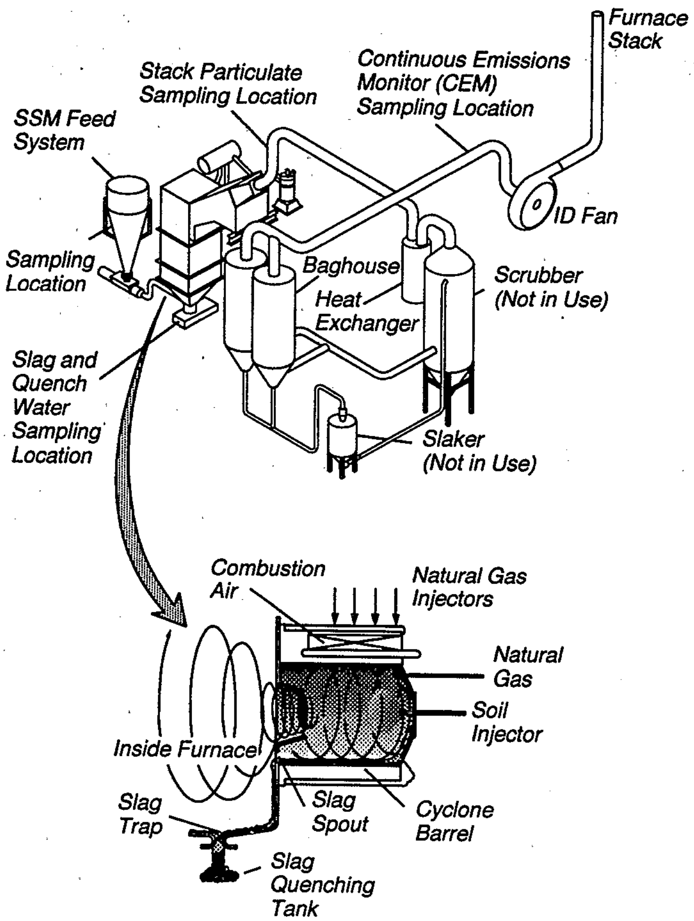

Figure 1. *Cyclone furnace facility with detail of the cyclone furnace barrel.*

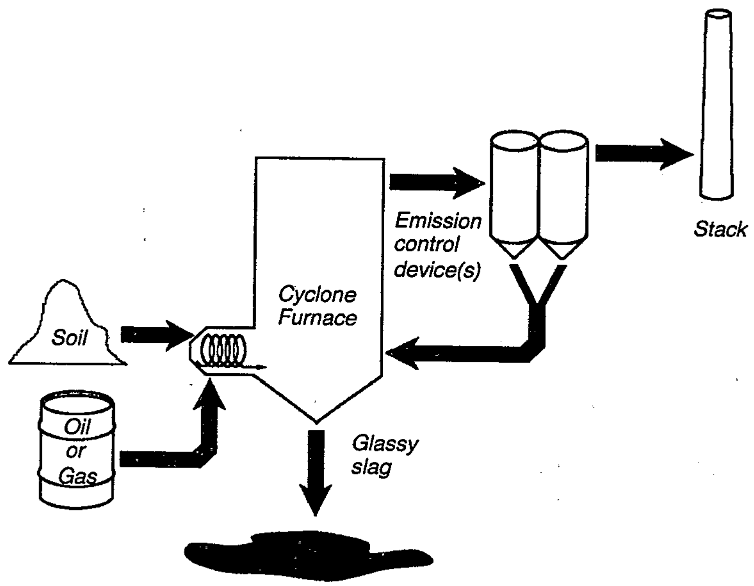

Figure 2. *Cyclone vitrification process.*

Materials and Methods

Synthetic Soil Matrix

A synthetic soil matrix formulated by EPA was used for all cyclone testing. Both clean and spiked SSM were obtained from the EPA Risk Reduction Engineering Laboratory (RREL) Releases Control Branch in Edison, NJ. SSM, used by EPA for treatment technology evaluations, has been well-characterized in previous studies (1). Clean soil was used for furnace conditions optimization. The spiked SSM used in the Emerging Technologies projects contained 7,000 ppm (0.7%) lead, 1,000 ppm (0.1%) cadmium, and 1,500 ppm (0.15%) chromium. The SSM used in the SITE Demonstration contained 7,000 ppm lead, 1,000 ppm cadmium, 4,500 ppm strontium, and 4,500 ppm zirconium.

Typical Run Conditions

Typical run conditions for the Phase I and Phase II tests are given in Table 1.

Sampling and Analysis

Sampling and analysis followed guidelines in the U.S. EPA SW-846 Manual, and the Quality Assurance Project Plan met RREL Category III requirements. Phase I and Phase II sampling locations for measurements and analyzers are shown in Figure 3.

Results and Discussion

The Phase I and Phase II Emerging Technologies projects were conducted using approximately 6 tons of unspiked SSM and 5 tons of SSM spiked with heavy metals. Phase I tests were conducted with dry SSM and Phase II tests with wet SSM (26% moisture). Stable cyclone operation was achieved during the several pilot tests, which ranged from 3 to 14 hr in duration. Particulate loading data and materials mass balance suggested from 95% to 97% of the input SSM was incorporated within the slag. Using natural gas as the fuel, the CO, CO_2, O_2, and NO_x stack emissions gases from the process were within acceptable ranges (<30 ppm, 11.5%, 1%, and <400 ppm, all corrected to 3% oxygen). The NO_x levels can be readily reduced by NO_x control technologies.)

The slag (vitrified soil) from the tests appeared to be a black, glassy, obsidian-like mass. Some large white glass particulates are readily visible in the slag fragments. When viewed under a low-magnification microscope, both the slag (soil) matrix and the embedded white particles appeared to have completely melted. The vitrified material can be easily crushed.

Table 1. *Typical Cyclone Furnace Test Conditions*

Condition	Typical Range of Values
Heat Input (natural gas fuel)	5 million Btu/hr
SSM Feed Rate	50 to 300 lb/hr
Excess Oxygen at the Stack	1.0%
Primary and Secondary Air Temperature	830°F
Slag Temperature	2370 to 2460 °F
Furnace Exit Gas Temperature	2800 to 3000 °F
Flue Gas Exit Temperature	2100 to 2200 °F
Baghouse Temperature	<200°F

TCLP Results

TCLP results for the Phases I and II heavy metals tests are shown in Figure 4. For both Phase I and Phase II, the untreated SSM exceeded the TCLP limits for lead and cadmium by >10X. Chromium, spiked at a level similar to lead and cadmium, did not exceed the TCLP limits (a similar phenomenon was reported in Ref. 1, and during the SITE Demonstration). The treated SSM was about 10X lower than TCLP limits for the three metals. The results show that the cyclone vitrification process always succeeded in producing a non-leachable slag.

Volume Reduction

Approximately 35% and 25% volume reduction (dry basis) was obtained by vitrification of dry SSM (Phase I) and wet SSM (Phase II), respectively. The volume reduction is a combination of 22% mass reduction, mainly attributed to the calcination of the limestone component of SSM, and the increased bulk density from 80 lb/cu ft for SSM to 86 to 92 lb/cu ft for the slag.

Fate of Heavy Metals (Mass Balance)

A mass balance for total ash, cadmium, chromium, and lead was performed for the cyclone furnace treatment process. The purpose of the mass balance was to determine the fate of the heavy metals during soil treatment. The heavy metals could be retained in the glass-like slag or be volatilized and leave the cyclone with the flue gas.

For the Phase I tests, the overall mass balance accounted for 79% to 103% of the total materials input to the furnace and the heavy metals mass balances accounted for 65% to 77% of the lead, 56% to 61% of the cadmium, and 141% to 145% of the chromium input to the furnace. In the case of chromium, mass balances in excess of 100% were calculated. The most likely source of excess chromium was a newly-installed refractory which contains 9.8% chromium oxide (Cr_2O_3), with "bake-out" or abrasion of the material causing the elevated stack chromium levels.

For the Phase II tests, the overall and heavy metals mass balances were closer to 100% of the materials input to the furnace. The overall mass balance achieved 102% to 107% of the total material input to the furnace, and the heavy metals balances achieved 74% to 87.5% for lead, 50.5% to 71.5% for cadmium, and 78.9% to 96.8% for chromium input to the furnace. (This time, the use of chromium

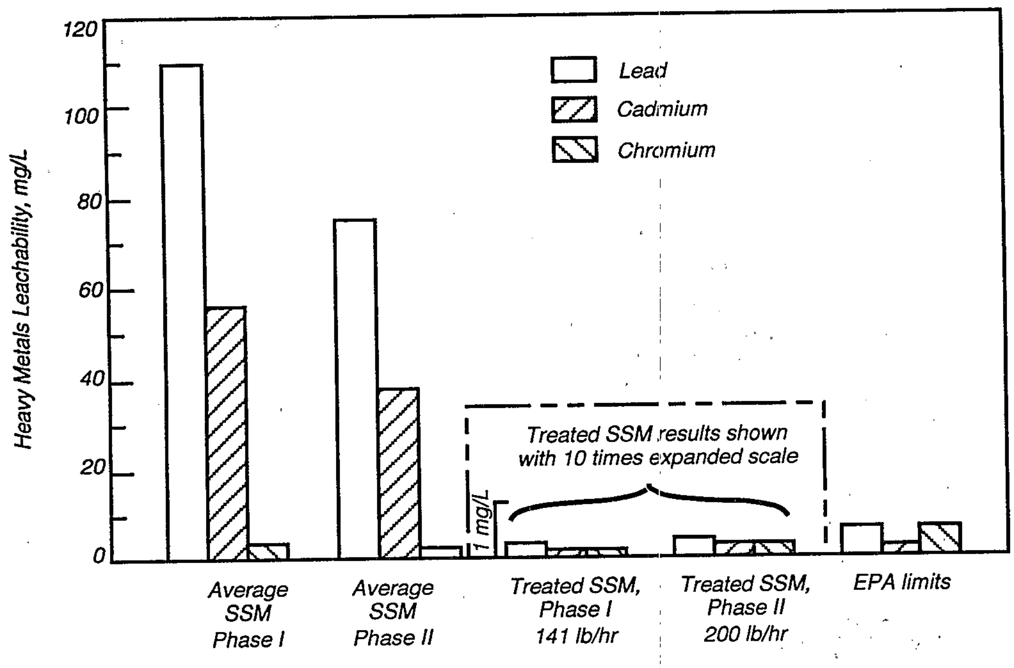

Figure 3. *Toxicity Characteristic Leaching Procedure (TCLP) results.*

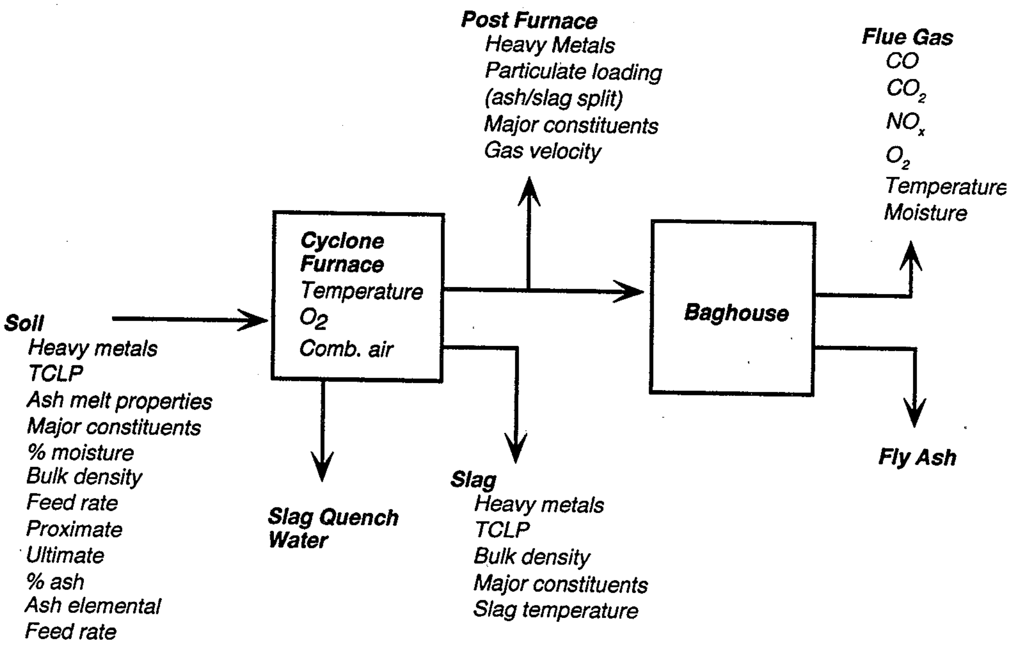

Figure 4. *Sampling locations and analyses.*

refractory was minimized to prevent any chromium contamination.)

A mass balance was calculated for each test as follows: The total flyash and slag streams were measured and normalized to 100%. The non-normalized mass balance was calculated from the percent flyash and the flyash metals concentration and from the percent slag and the slag metals concentrations. The mass balance was also normalized (100% = amount of heavy metals measured in the input SSM calculated from the feed rate and the SSM metals concentration). The amount of cadmium captured in the slag was 8% to 16% and 12% to 23% (Phase I and II data, respectively); lead captured in the slag was 24% to 35% and 38% to 54%; chromium captured in the slag was 80% to 95% and 78% to 95%.

The heavy metals content in the slag increases with increasing SSM feed rate between 50 to 300 lb/hr. Since fuel (natural gas) feed was relatively constant, this suggests that increasing SSM feed rate reduces the solids residence time in the furnace (and lowers measured slag temperatures) and consequently reduces vaporization of heavy metals into the flue gas. This is a promising trend for full-scale operation.

An attempt was also made to correlate the different behavior of the metals during cyclone treatment with their volatility. The temperature at which the metal vapor pressure was 100 mm Mercury was chosen as the volatility parameter. The percentage of heavy metals retained in the slag was a function of volatility of the metal for the Phase I, Phase II, and demonstration tests. These results suggest that the cyclone vitrification process will show high capture for very low volatility contaminants such as many radionuclides (e.g., zirconium, uranium, thorium). Conversely, high volatility metals are likely to be concentrated in the flyash, which may then be suitable for recycle to the cyclone furnace or possible metal recovery.

Conclusions

The Babcock & Wilcox 6 million Btu/hr pilot cyclone furnace was used successfully to

- Vitrify an EPA Synthetic Soil Matrix (SSM) spiked with 7,000 ppm lead, 1,000 ppm cadmium, and 1,500 ppm chromium.
- Produce a non-leachable (TCLP) product.
- Incorporate from 95% to 97% of the input SSM within the slag.
- Maintain stable cyclone operation.
- Using natural gas as the fuel, produce CO and NO_x stack emissions gases from the process within acceptable ranges.
- Increase the capture of heavy metals in the slag with increasing feed rate and with decreasing metal volatility.
- Reduce the volume of the synthetic soil matrix by 25% to 35% (dry basis).

Because the projects were conducted on a pilot cyclone furnace configured as a utility boiler for proof of concept of testing, and by no means optimized for soil vitrification, a unit designed for dedicated soil vitrification may improve process throughput and performance. In November of 1991, a SITE Demonstration was successfully conducted to provide performance and cost information for mixed waste (organics, metals, and simulated radionuclides). The next steps in the technology development include design, construction, and field demonstration of a full-scale unit.

References

1. P. Esposito, J. Hessling, B. Locke, M. Taylor, M. Szabo, R. Trumau, C. Rogers, R. Traver, and E. Barth, 'Results of Treatment Evaluations of a Contaminated Synthetic Soil," *JAPCA*, 39: 294 (1989).

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The complete report, entitled "SITE Emerging Technologies Project : Babcock & Wilcox Cyclone Vitrification," (Order No. PB93-163038; Cost: $9.00, subject to change) will be available only from:
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