BENEFICIAL USE OF LOWER FOX RIVER CONTAMINATED SEDIMENT

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ABSTRACT

During the comment period of the 2001 draft of the Lower Fox River Remedial Investigation/Feasibility Study (RI/FS), WDNR and Minergy Corp, completed the evaluation of the cost and treatment-effectiveness of a vitrification technology based on standard glass furnace technology, to treat contaminated sediment. The three phases of the study were: I) Mineralogy and sediment characterization; II) Crucible melt and preliminary design engineering; and III) Pilot-scale sediment melt of dewatered dredge material. Phase III was completed in August 2001. During Phase III, approximately 50 tons of dredged and dewatered river sediment was processed through a glass furnace specifically designed and built for treating sediments from the Lower Fox River. This phase clearly showed that the glass furnace technology created a quality glass aggregate material from river sediments. The properties of the glass aggregate were quite positive and were very consistent, producing a hard, dark, granular material with exceptional beneficial re-use potential and value.

All input and waste streams were sampled during the pilot. Testing was preformed for a wide range of chemicals including PCB congeners, dioxan/furans, semivolatile organic compounds, volatile organic compounds, and heavy metals. The glass aggregate was subjected to both ASTM water leaching procedures and SPLP procedures. Results of the testing showed that on a stack basis >99.9999% of the PCB was destroyed, achieving the destruction efficiency required under the Toxic Substances Control Act (TSCA). The results of the glass aggregate leach testing showed the material passed standards used by WDNR to grant a Low Hazard Exemption from solid waste rules for this material.

Final unit cost will depend on the beneficial re-use of the material and the value in those markets. However, even with a nominal resale value of $2 ton/glass the unit cost for this technology is significantly less that other commercially available thermal treatment technologies. Unit cost for the most effective treatment of the tonnage of sediment estimated to be removed from Operable Units 3 and 4 of the Lower Fox River ranges from $32 to $41/ton dredged and dewatered sediment (assuming 55% solids). This unit cost does not include dredging and dewatering and therefore is functionally equivalent to a tipping fee at a landfill.

Keywords: vitrification, sediment treatment, beneficial uses

INTRODUCTION

Minergy Corp. (Minergy), in response to the release of the 1999 draft of the Lower Fox River Remedial Investigation/Feasibility Study (RI/FS) by the Wisconsin Department of Natural Resources (WDNR), offered comments regarding the use of thermal treatment technologies included in the FS. Minergy suggested that inefficient technologies were used in preparing the various remedial alternatives and that they believed vitrification and the use of Glass Furnace Technology (GFT) was more appropriate and cost effective approach to treating Lower Fox River sediment. Following discussions with WDNR resulted in Minergy preparing a proposal for a multi-phased study to determine the treatment and cost effectiveness of GFT to treat PCB contaminated sediment from the Lower Fox River. The proposal offered that during the process to produce a high quality glass aggregate, which has resale and beneficial re-use value, the GFT would not only destroy organic contaminants (primarily PCB) but also immobilize inorganic contaminants (primarily heavy metals) producing a final aggregate product that is very inert.

Minergy proposed to WDNR a four phased feasibility study for the testing of GFT process and included a provision to cost-share the study. Minergy's initial four phases of the study were:

- Phase I: Mineralogy and sediment characterization
- Phase II: Crucible melt and preliminary design engineering
- Phase III: Pilot-scale sediment melt of dewatered dredge material (2 tons/day glass aggregate for 14 days)
- Phase IV: Full-scale facility construction.

With funding assistance from US EPA's Great Lakes National Program Office (GLNPO), WDNR contracted Minergy to conduct the GFT Feasibility Study. Also, recognizing the extreme scrutiny PCBs have been under and the need for a thorough independent evaluation of contaminant fate, especially during Phase III, WDNR requested assistance from US EPA Superfund Innovative Technology Evaluation (SITE) Program. The SITE Program agreed to independently undertake the evaluation of cost and treatment effectiveness for this project.

During the comment period of the 2001 draft Lower Fox River RI/FS, Minergy completed the project to evaluate the feasibility of the GFT, to treat PCB contaminated sediment from the Lower Fox River. In addition to the GFT feasibility study, Minergy also under took several other studies including; 1) a unit cost study (Minergy 2003a), 2) a permitting review (Minergy 2003b); and 3) sediment handling characterization (Minergy 2003c). Collectively these reports, in addition to the Sediment Melter Final Report (Minergy 2001) and data collected by US EPA SITE Program, which will be summarized in an Innovative Technology Evaluation Report (ITER), form the basis for evaluating the cost effectiveness and efficiency of this technology to treat PCB contaminated river sediment.

SUMMARY OF PHASES I AND II

Phase I testing characterized the mineral composition of river sediments to estimate the glass quality, durability and melting point. Sixteen archived river sediment samples, representing the entire 39 river miles, that were collected during previous investigations, were analyzed for mineral composition and loss on ignition (LOI) (Table 1). The mineral composition of the river sediments was very consistent throughout the river and is very favorable for producing a quality glass product. The low results generated in the LOI tests confirm that a melting technology is more appropriate for river sediments than an incineration technology. With these positive results in hand, the project moved into Phase II.

Table 1. Mineral and LOI Analysis of River Sediment

Chemical Analysis	Phase I Samples Average ($\pm$SD) %	Phase III Batches Average ($\pm$SD) %
Na_2O	0.73 (0.12)	0.44 (0.5)
MgO	6.21 (1.87)	9.79 (0.74)
Al_2O_3	11.34 (3.04)	9.72 (0.26)
SiO_2	63.73 (8.45)	36.56 (1.42)
P_2O_5	0.32 (0.16)	0.36 (0.01)
K_2O	3.05 (0.45)	1.73 (0.1)
CaO	8.36 (3.07)	35.49 (2.2)
TiO_2	0.6 (0.27)	0.7 (0.2)
Fe_2O_3	4.56 (1.46)	3.21 (0.78)
LOI @750^{o}C (% dry basis)	8.59	9.1

During Phase II, crucible melts of Lower Fox River sediment were conducted to determine the actual melting conditions and glass characteristics/qualities of the sediment alone and when augmented with other materials (flux mixtures). Fluxes are added to the batch material to optimize the mineral composition, which in turn minimizes the amount of energy necessary to melt the material. The four different "recipes" were tested and all successfully melted the sediment into glass. The addition of limestone, as a fluxing agent, to the sediment provided the best results. Phase II results included a proposed recipe for melting river sediment into glass aggregate and preliminary engineering designs for the pilot test facility proposed for Phase III. This preliminary engineering recommended not using an existing glass furnace for Phase III testing. Results of Phase II testing indicated that:

- The cost to retrofit an existing facility to the specification needed to melt sediment would be as much as building a pilot melter to these same specifications,
- Most existing facilities are too large to accommodate a limited duration test and would not provide the ability to adequately sample the various waste streams to determine destruction efficiency, and
- Use of oxy/fuel burners would be most energy and cost efficient.

Together, the results of Phase I and II indicated that the glass furnace construction and operating costs could allow the processing and melting of the river sediments to be considered an economically viable option. Therefore, Minergy and WDNR initiated Phase III, the construction and operation of a pilot scale glass furnace, specially designed to generate the operational data, treatment effectiveness data, and cost information needed for scale-up to a full-scale facility (Phase IV).

PHASE III: PILOT SCALE MELT

Phase III Objectives

WDNR, Minergy, US EPA GLNPO and US EPA SITE collectively agreed that there were two primary objectives of Phase III testing (EPA 2001):

P1. To determine the treatment efficiency (TE) of PCBs in dredged-and-dewatered river sediment when processed in the Minergy GFT.

P2. To determine whether the GFT glass aggregate product meets the criteria for beneficial reuse under relevant federal and state regulations.

In addition three secondary objectives were identified (EPA 2001):

S1. Determine the unit cost of operating the GFT on dewatered dredged river sediment.

S2. Quantify the organic and inorganic contaminant losses resulting from the existing or alternative drying process used for the dredged-and-dewatered river sediment.

S3. Characterize organic and inorganic constituents in all GFT process input and output streams. Of principal concern is the formation of dioxin and furan during the vitrification step.

Phase III Design and Operations

The GFT process actually consists of two basic steps: a sediment-drying step followed by the vitrification (melting) step. Due to the potential to release contaminants during both steps and the limited scale of Phase III, it was necessary to evaluate these two steps independently. Both processes were independently evaluated by US EPA SITE program. The evaluation of the drying step was completed using a bench scale Holoflite® dryer at Hazen Research Inc.'s Golden, Colorado facility. Results from the dryer will not be discussed further because the waste streams from this process can and will be incorporated directly into the design of the melter thus effectively treating these waste streams. However, the dryer evaluation did provide some insights into the material handling characteristics of the sediment including:

- Fox River sediments can be physically modified to provide flowable feed to a dryer,
- The amount of moisture in the sediments can be reduced to <10%,
- Heat transfer coefficients and thermal efficiencies,
- Dewatered sediment exhibited stickiness or agglomerating characteristics at < 65% solids, and
- Dewatered sediment > 65% solids did not exhibit a sticky or agglomerating characteristics.

Many of these characteristics have been evaluated further in subsequent work preformed by Minergy under contract to WDNR (Minergy 2003c) and incorporated into the design of a full-scale facility.

Process Design

The glass furnace (melter) was designed for Minergy by Frazier-Simplex based on the results obtained from Phases I and II (Figure 1). The pilot-scale glass furnace is simply a refractory-lined rectangular melter. The refractory is brick or concrete that has been specially treated to resist chemical and physical abrasion, has a high melting point, and provides a high degree of insulating value to the process. The melter has a melting area of 10 ft^2, and was designed to produce 2 tons per day of glass.

Natural gas is fired in the furnace, raising the internal temperatures to between 2600 to 3000^o F. The melter has a maximum natural gas firing rate of 1.70×10^6 Btu/hr, and a maximum design oxygen consumption rate of 3500 SCFH. Exhaust treatment is simplified and energy efficiency improved by the melter's use of purified oxygen (oxy-fuel) rather than ambient air as the oxygen source. Due to low gas volumes produced by the oxy-fuel melter and the large volume of gas space above the molten line, gases remain resident in the melter for a significant period of time (~2 seconds at the pilot scale).

A motor driven screw charger was used to feed the melter. The screw charger was water cooled to allow insertion into the melter. The screw charger is mounted on rails to allow for quick and easy removal from the furnace. A variable speed A.C. motor drive is used to drive the screw charger, and is used to control feed rate into the melter.

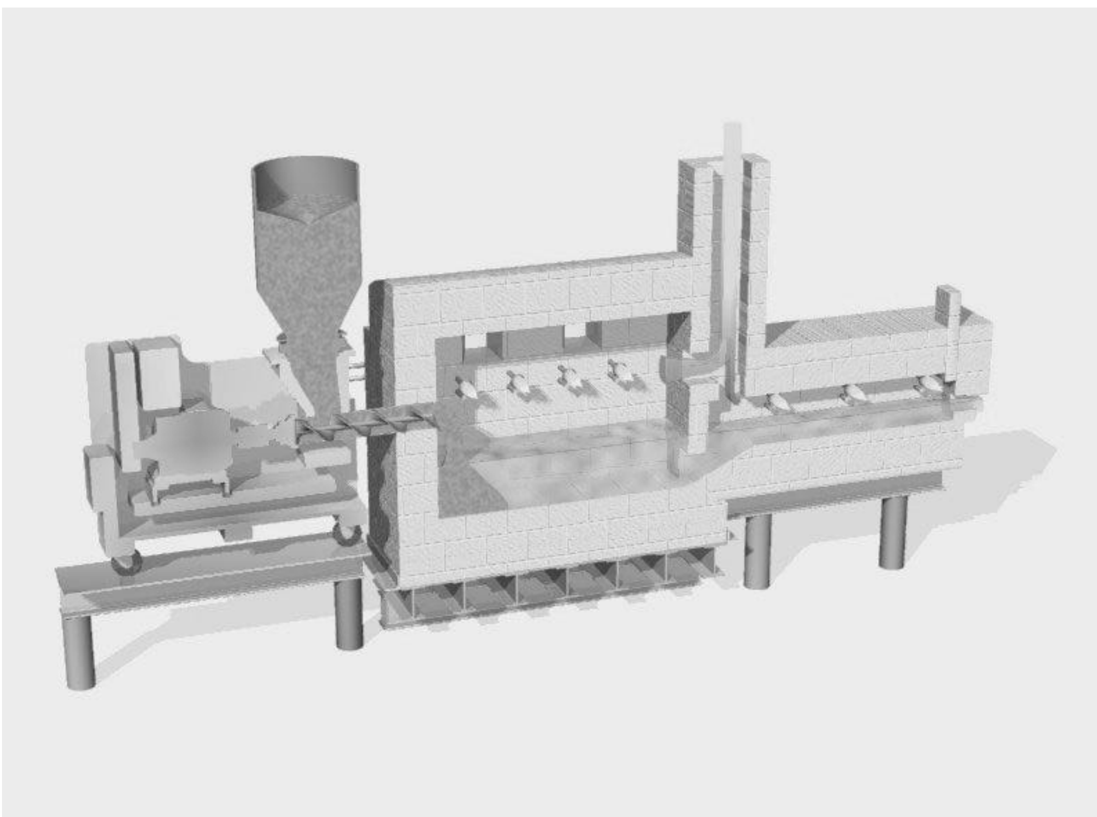

Figure 1. Cross Section Through Pilot Scale Melter

At these temperatures, the sediment melts and flows out of the furnace as molten glass. Molten phase glass product was discharged into a 600-gallon water-filled quench tank. Quench tank water is constantly circulated and cooled to maintain water temperatures below 120 ^{o}F. A screw conveyor was used to constantly extract and de-water the frit glass from the quench tank. Finished frit glass was transferred into 55 gal metal drums.

A split stream of the 2800 ^{o}F exhaust gas from the melter was treated in a pilot scale air quality control system (not included in Figure 1). The apparatus consisted of a gas cooling section, wet scrubber and an activated carbon filter. Initially the melter exhaust gas is cooled from 2800 ^{o}F to 400 ^{o}F. Initial gas cooling was accomplished by indirect cooling to simulate gas temperature / time profiles similar to incinerators with heat recovery. The wet scrubber consisted of a packed tower filled with stainless steel packing. Cooling water is used to reduce the exhaust gas temperatures to approximately 100 ^{o}F. Cooled exhaust gas was processed in a bed of activated carbon. The primary purpose of the activated carbon bed is to achieve mercury removal. A centrifugal blower and control valve proper air flow through the air quality control equipment. Sampling taps were installed after the gas cooling section and after the activated carbon filter.

Process Operations

The melter was operated on a continuous basis for one week to allow adequate time to collect all of the air samples required. The melter was fed at an average feed rate of 224 pounds per hour. The average rate of glass production was 1.7 tons per day. Melter operating temperatures ranged from 2750 to 2930 ^{o}F. The average melter temperature during the testing was 2825 ^{o}F. Melter natural gas input rates averaged 748,000 Btu/hr on a higher heating value basis (HHV). Oxygen consumption averaged at 2098 SCFH. Oxygen flow rates were biased due to the organic content in the sediment. In glass furnaces processing organic free feed material, the typical ratio is 2.1 cubic feet of oxygen per cubic foot of natural gas (with a GCV of 1000 Btu/ft^{3}). The oxygen to natural gas ratio for the test was maintained at 2.8 cubic foot of oxygen per cubic foot of natural gas, to result in an average outlet (stack) oxygen content of 15.36 % O_2 on a dry basis.

Process Feed Material Properties

River sediment for the pilot testing was obtained from the 1999 dredging operation conduced on a section of the Lower Fox River designated as Sediment Management Unit 56/57 (SMU 56/57). During this operation, the dredged sediment was first conditioned to remove debris, stone and sand. The sediment was conditioned with lime and sent to a plate and frame filter press for de-watering. Approximately 68 tons of dredged and dewatered sediment was set aside for the Phase III testing. The sediment was received at typical moisture content of 48% to 52% expected for this dewatering process. The sediment was further dried to a moisture content of 5% to 18% by using a low temperature electric barrel oven.

The dried sediment was finely grained material (Table 2). The entire lot of sediment set aside from the dredging project was dried and bagged as 30 separate batches. To determine if there was any variability in the mineral content between each lot of material, 30 samples of the sediment were taken and analyzed for major metal oxide content (Table 1). The loss on ignition procedure (LOI) was performed at 1000 ^{o}C for 4 hours to also assure decomposition of all carbonates in the lime stone fraction of the sample. The results of the LOI testing ranged from 27.2% to 30.8%. The gross calorific value (GCV) was measured at 1376 Btu/lb, and the organic content is estimated at 5.5% to 9.0%.

Table 2 Sediment particle size distribution

Size, micron	% passing
6300	96
2000	88
850	85
420	83
200	80
75	68
33	63

PHASE III SAMPLING RESULTS

Although USEPA SITE Program has not completed the ITER for this demonstration, they have released the validated results of the chemical testing they conducted during Phase III. As described in the Quality Assurance Project Plan (EPA 2001), all input and waste streams were sampled during the pilot. Testing was preformed for a wide range of chemicals including congener PCB (n=78), dioxan/furans, semivolatile organic compounds (SVOCs), volatile organic compounds (VOCs), and heavy metals. In addition, the glass aggregate was subjected to both ASTM water leaching procedures and SPLP procedures to determine benefical re-use. Approximately 190 individual samples were collected from all possible waste streams during the August 2001 pilot.

The sediment charged into the melter during the pilot testing averaged 28 mg PCB/kg. Exhaust gas emissions were sampled on the pilot melter before and after the air quality control equipment. The average PCB concentration of the exhaust after the air quality control equipment was 35.1 ng/dry standard cubic meter (DSCM). In comparison, the average PCB concentration of the exhaust before the air quality control equipment was only slightly higher at 45.9 ng/DSCM. Thus, on an hourly average post-air quality control stack basis this equates to a PCB destruction of >99.9999 % during the pilot.

The formation of dioxins and furans during the thermal treatment of PCB contaminated sediment was identified as a major concern during the development of the sampling plan. Therefore, dioxin and furan were sampled in all waste streams. On average the sediment contained 23.5 and 65.6 ng/kg 2,3,7,8 TCDD (dioxin) and 2,3,7,8 TCDF (furan), respectively. No 2,3,7,8 TCDD was detected in either the pre- or post air quality control equipment or glass aggregate samples. 2,3,7,8 TCDF was detected only in the post air quality control equipment at an average of 0.0018 ng/DSCM. On an hourly average basis during the pilot, 8815.5 ng of 2,3,7,8 TCDD and 2,3,7,8 TCDF were loaded into the melter while less than 0.1 ng of only 2,3,7,8 TCDF was released in the exhaust. This not only represents a significant reduction in 2,3,7,8 TCDD/TCDF but more importantly the data demonstrate that these compounds are not created to any extent during this treatment process.

The glass aggregate also demonstrated acceptable characteristic for beneficial reuse. The glass aggregate did not exceed any of the criteria specified to determine beneficial re-use that were identified in the project QAPP (EPA 2001). In fact, the ASTM water leach test and SPLP test did not detect any 2,3,7,8 TCDD or TCDF, not a single PCB congener, any SVOCs nor any of the eight heavy metals.

Mercury was another contaminant of significant concern. Mercury concentrations in the sediment averaged 0.7 mg/kg. All glass aggregate samples analyzed for mercury resulted in no detections as did all the exhaust samples.

Using the results from the pilot melter, the emissions from a 250 glass ton per day full-scale facility were calculated. A multi-media permitting review concluded that a commercial-scale GFT facility could be constructed and operated in compliance with all existing applicable environmental regulations and standards (Minergy 2003b).

UNIT COST

The Glass Furnace Technology incorporates and optimizes several factors to achieve greater cost and treatment effectiveness' than other thermal processes, including rotary kilns. These factors include:

- Oxy-Fuel. The use of pure oxygen (rather than atmospheric oxygen) and natural gas has the added benefits of:
    - Substantially reducing pollutant emissions thereby reducing capital and annual operating expenses associated with air quality control equipment
    - Higher heat transfer and thermal efficiencies which together increase throughput in an existing facility or reduce the size of new facilities (see Baukal 1998 for a review of oxy-fuel combustion)
- The use of highly insulating refractory. A glass furnace is able to utilize several layers of refractory brick thus increasing the insulating value and keeping the oxy-fuel heat inside the furnace. In comparison, other thermal processes like rotary devices for vitrification can have thinner refractory linings and thus may have up to 3 times the amount of heat loss.
- Use of a dryer to remove water from the sediment. Many other technologies process wetter material and therefore a substantial portion of the energy consumption is used in heating water to the same temperature as the sediment. Thermal recovery from the glass furnace can provide a significant portion (85%) of the energy to pre-dry sediment before introduction into the glass furnace.

In response to USEPA SITE Program's need to also determine the cost of the technology, Minergy performed a Unit Cost Study for Commercial-Scale Sediment Melter Facility (Minergy 2002). The Unit Cost report has subsequently been revised (Minergy 2003a) based on the additional work Minergy completed on sediment handling characteristics (Minergy 2003c). This report used standard build-up estimating approaches in developing the cost estimates. This approach uses the information generated in Phases I, II and III and on that basis requested relevant cost, performance and sizing data from equipment suppliers and contractors. With this data, the general plant layout (Figure 2), mass and energy balance and equipment arrangements were made. Estimates were done for construction and operations and through financial modeling, a unit-cost forecast. The base case estimates were made using a plant size of 250 glass tons per day. Sensitivity analysis was also conducted for various sized melter plants, with and without integrated storage, different sediment moistures, a range of glass aggregate resale values, and several different project durations. Assuming a full-scale facility was constructed to handle all the sediment to be removed from Operable Units 3 and 4 of the Lower Fox River site in a 10 year time period the unit cost for treatment is estimated to range from $32 to $41 per ton of dredged and dewatered (55% solids) sediment. The full range of unit costs estimated to treat the same quantity of sediment, given all the possible combinations developed in the sensitivity analysis is between $15 to $57.

Final unit cost will depend on the beneficial re-use of the material and the value in those markets. However, even with a nominal resale value of $2 ton/glass the unit cost for this technology is significantly less that other commercially available thermal treatment technologies.

BENEFICIAL REUSE OPPORTUNITIES

Chemical composition of the glass aggregate and its vitreous texture suggested that the material may possess the latent cementitious properties and be used as an active mineral admixture in cements and concretes.

Ordinary portland cement is produced by pulverizing clinker, the fused product of high-temperature treatment consisting essentially of hydraulic calcium compounds, with a small amount of gypsum. Blended cements may contain, besides clinker, supplementary cementitious materials, or active mineral admixtures. The latter are siliceous or siliceous and aluminous materials that possess little or no cementitious value but which chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.

These materials are beneficial to the performance of concrete, in that by their physical and chemical composition, they take part in the hydration reaction of portland cement. They consume some less desirable by-products of cement hydration, and produce desirable calcium silicate hydrate, thus improving the microstructure and properties of the paste.

The following tests were then conducted on ground glass aggregate samples to determine performance as a cementitious material:

- Slag activity index according to ASTM C 989-99, "Standard Specification for Ground Granulated Blast-Furnace Slag for Use in Concrete and Mortars"

- Strength Activity Index according to ASTM C 311-00, "Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland-Cement Concrete"

Mortar cubes were prepared to assess the performance of blends with 0%, 20% and 50% of the cement mixture being replaced by glass aggregate. The water required to achieve equivalent workability to the control mix decreased slightly with increasing glass content. This is considered beneficial because less chemical admixture will be required in a concrete mixture containing glass aggregate.

The results of the testing were very positive. The strength of the mortar mixes containing 20% glass were within the limits required by ASTM C 618. The results therefore indicated that the material had potential to perform as material at dosages of about 20% cement replacement. The great majority of the intended cement replacement market would be at 20% substitution. However, the glass aggregate displayed suitable 28-day strengths for as high as 50% replacement. More research is needed to optimize the blend compositions. The optimization parameters would include the cement/glass ratio, fineness, and cost factors.

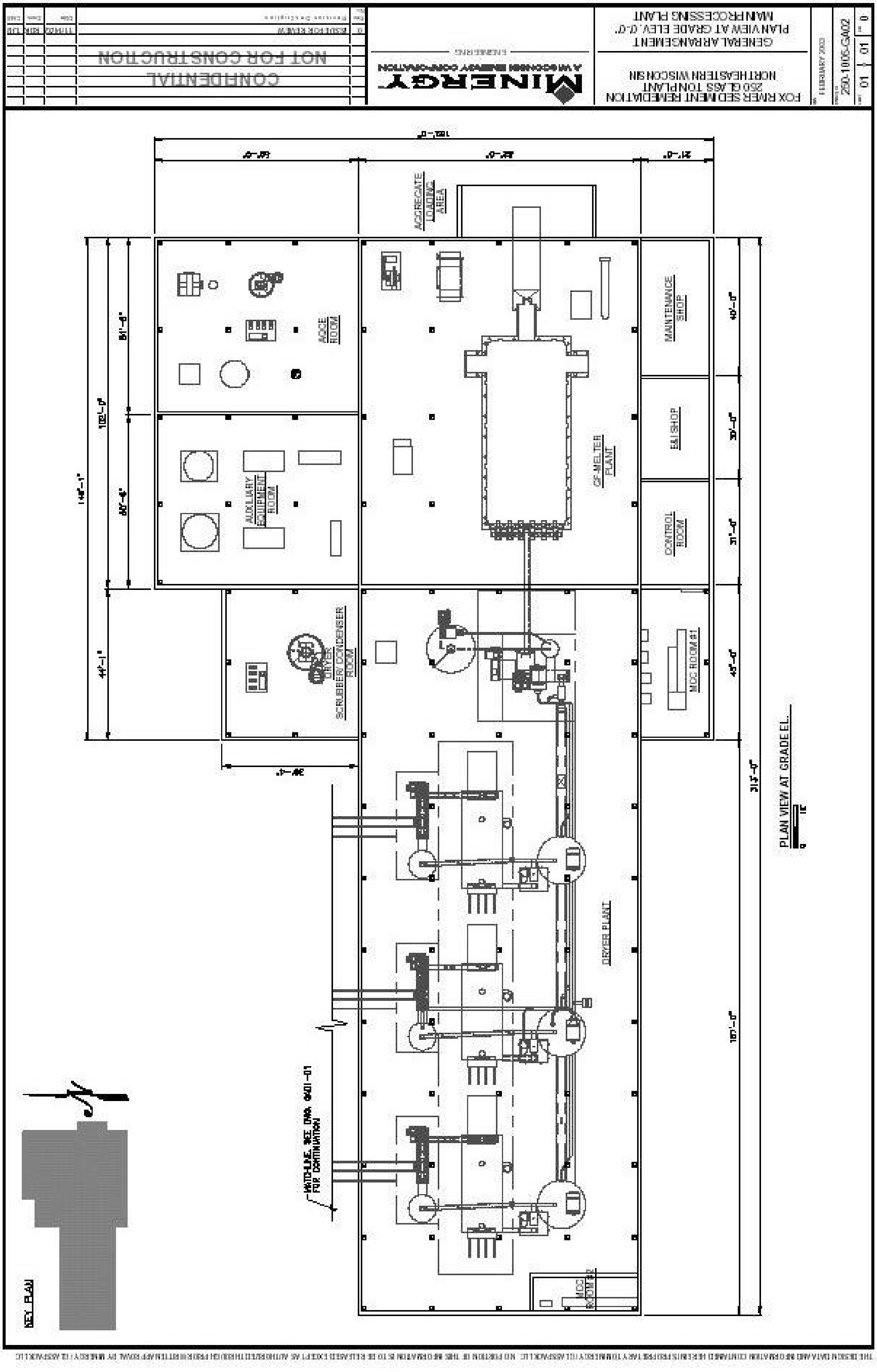

Figure 2. General Plant Arrangement of 250 Glass Ton/Day Facility

In addition to the use of crushed glass aggregate made from river sediment as a pozzolan replacement in concrete, other potential uses that have been evaluated include:

- Roofing shingle granules
- Industrial Abrasives (sand blasting grit)
- Ceramic Floor Tile
- Construction fill material
- Material for *in situ* capping of remaining contaminated sediment

The results of testing done to date on the glass aggregate was submitted to the WDNR requesting a Low Hazard determination under Wisconsin solid waste statutes. WDNR has granted Minergy a Low Hazard Exemption for glass aggregate produced from Lower Fox River sediment by the GFT process. This exemption eliminates the regulation of this material under Wisconsin solid waste rules although it restricts its use to certain approved beneficial re-use options.

CONCLUSION

The results of the pilot test indicated that PCB contaminated river sediment can be successfully converted into a vitrified glass aggregate product that is environmentally acceptable for beneficial reuse. Organic contaminants such as PCB are effectively destroyed during the process and the GFT process in particular does not result in formation of dioxin or furans, which is a concern, raised by the local environmental community. Both environmental and process performance data quality was acceptable. The performance data is suitable to allow for scale up to a larger commercial scale type project. The glass aggregate end product can be use for many industrial applications or it can be ground and utilized in a blended cement product meeting ASTM specifications for blended cements. The GFT is cost competitive with other thermal treatment technologies and if one considers the added benefit of permanent contaminant destruction, can be also be competitive with landfill disposal.

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