OVERVIEW OF MINERGY’S GLASSPACK® VITRIFICATION TECHNOLOGY

MINERGY®
VITRIFICATION

INTRODUCTION

Vitrification, defined as a thermal process for converting minerals into glass, is an emerging technology in the area of treating wastewater residuals. Vitrification has a well established track record in other industrial processes especially glass furnaces used in the glass manufacturing industry and slagging furnaces used in coal-fired power generation.

Wastewater treatment residuals, such as paper mill sludge and biosolids, possess characteristics common to both glass manufacturing and power generation and therefore play two important roles in the vitrification process. First, the organic fraction provides the thermal energy required to complete vitrification. These organics are essentially a biomass fuel that is renewable through the cycle of water use and wastewater treatment. Secondly, the mineral fraction (ash, clays, and mineral fillers) melts into a glass aggregate product with multiple beneficial construction and industrial applications.

Until recently, commercial vitrification of waste materials has been limited to hazardous waste applications. Commercial scale vitrification of high-volume industrial wastewater treatment residuals emerged in 1998 with Minergy's Fox Valley Glass Aggregate Plant (FVGAP) located in Neenah, Wisconsin, USA. FVGAP vitrifies paper mill sludge from several local paper mills into a glass aggregate that is sold and used locally. FVGAP vitrifies approximately 350,000 tons of paper mill sludge into approximately 50,000 tons of glass aggregate annually. Significant interest in FVGAP lead Minergy to develop a second generation vitrification technology, GLASSPACK®, applicable for individual on-site processing of biosolids.

Process Description – GLASSPACK®

The GLASSPACK® system is a combination of two innovative concepts. The first is a patented closed-loop oxygen enhanced combustion process that uses enriched oxygen to achieve temperatures that promote vitrification, provide complete destruction of organic compounds, and reduce emissions. The high process temperatures completely melt the inorganic fraction into an inert beneficially reusable glass aggregate product.

The second innovation is the GLASSPACK® modular melter concept. The melter is a shop-fabricated unit that can be delivered to the construction site on a single truck shipment. The entire process is highly modularized to minimize footprint, field installation costs and construction schedule.

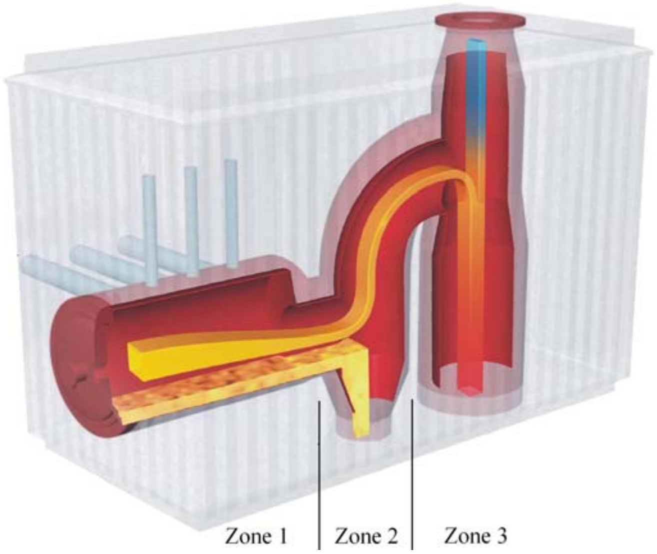
Closed-loop Oxygen Enhanced Combustion

Standard combustion technologies use atmospheric air as the source of the oxidizer (oxygen) even though atmospheric air contains only about 21% oxygen (O_2) and 79% nitrogen (N_2). Only the oxygen is needed for combustion while N_2 contributes nothing to the process. Minergy's patented closed-loop oxygen enhanced process uses pure oxygen (>90%) injection as the source of oxidizer, eliminating the use of atmospheric air and therefore the ballast and diluent N_2.

Oxygen enhanced combustion provides significant process benefits including higher radiant heat energy, higher thermal transfer efficiency, improved ignition characteristics and greater flame stability. These process efficiencies lead to greater heat transfer to the biosolids and produce the temperatures necessary to sustain the melting process.

At the heart of the process is the GLASSPACK® melter. GLASSPACK® features a 3-zone operation, comprised of separate but interconnected chambers:

- Zone 1: Melting Zone
- Zone 2: Phase Separation Zone
- Zone 3: Gas Cooling Zone



Zone 1: Melting Zone. Feedstock that has been pre-dried to at least 85% solids or more is injected along with synthetic air (a more detailed description of synthetic air is set forth below) into the Zone 1 chamber. In this zone, the organic component of the sludge is completely combusted, liberating a significant amount of heat energy and resulting in temperatures between 1315° and 1482° C (2400° and 2700° F). At these high temperatures, the mineral (ash) component of the feedstock melts to form a pool of molten glass at the bottom of the Zone 1 chamber. The high temperature environment is designed to provide very high destruction efficiencies of organic compounds that may be contained in the feedstock. In a typical municipal biosolids application, once the operating temperature is reached, the energy released from combustion of the biosolids is adequate to keep the process going, eliminating the continued need for co-fire fuel.

Zone 2: Phase Separation Zone. Phase separation of the molten glass and exhaust gas occurs by gravity draining the molten glass from Zone 1 through a drain port on the bottom of the Zone 2 chamber. The molten material drops into a water quench tank and is cooled into the glass aggregate product. The hot combustion gases are directed out of Zone 2 through a refractory lined duct into Zone 3.

Zone 3: Gas Cooling Zone. In this zone, hot exhaust gas is cooled through dilution mixing with lower temperature gases obtained external to the melter. A typical source of lower temperature dilution gas is recirculation flow from a closed–loop installation. The two primary benefits of reducing the exhaust temperature are to eliminate expensive refractory-lined ductwork exterior to the melter, and to cool any particulate carryover below the softening point, thus eliminating ductwork fouling. The temperature of the Zone 3 exit gas varies depending on the temperature and quantity of the dilution gas, but is typically in the range of 370 ° to 870 ° C (700 ° to 1600 ° F) Higher temperature exit gas can provide for higher efficiencies in downstream heat recovery process.

The combustion and melting process in GLASSPACK® is enclosed in an air tight gas path that prevents air infiltration and leakage of hot exhaust gases into the surrounding area. The gas path is internally lined with refractory to assist in maintaining the internal temperatures necessary for vitrification. Refractory material selection, thickness, and installation methods have been optimized for costs, heat loss, and serviceability. The entire gas path is surrounded by a water jacket to dissipate heat lost through the refractory.

Hot exhaust gases from the discharge of Zone 3 are ducted into a heat exchanger to recover thermal energy and generate low temperature dilution gas (Figure 2). A number of options are available for recovering the heat including steam generation, thermal oil, and hot gas heat exchangers.

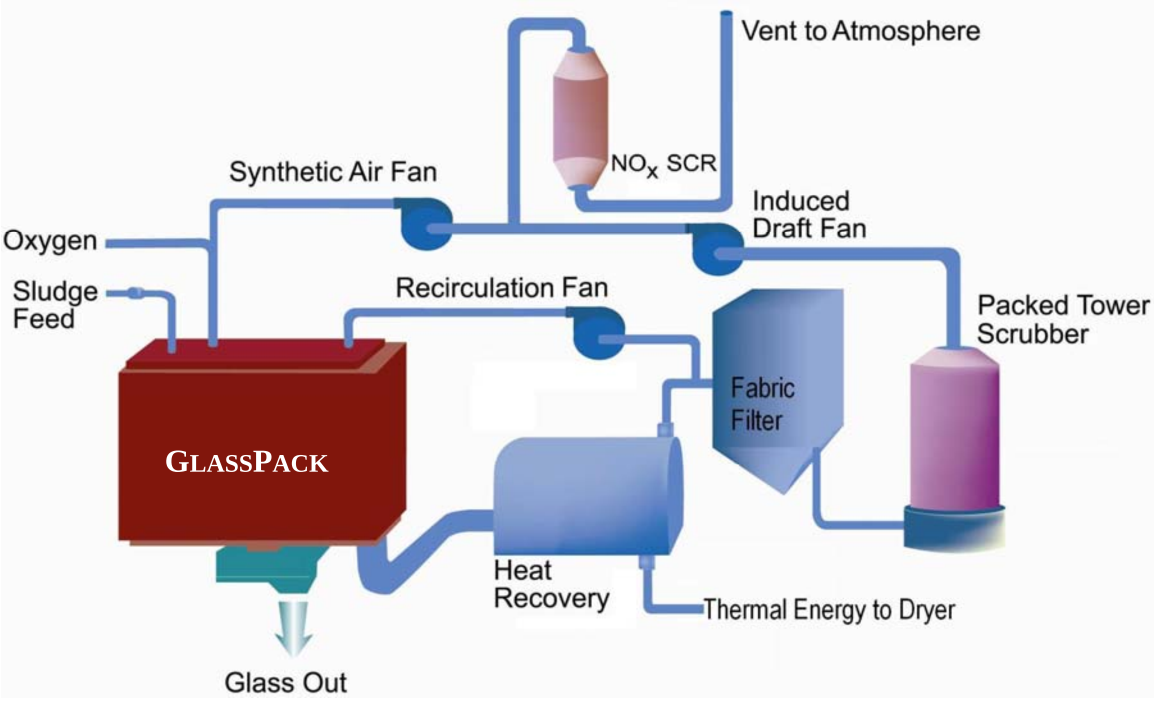


Figure 2. GLASSPACK Closed-loop Oxygen Enhanced Combustion Configuration

After exhaust gas exits the heat recovery unit, the exhaust stream is split into two directions. Approximately 70% of the exhaust gas flow enters the Exhaust Gas Recirculation (EGR) fan and is injected back into Zone 3.

The remaining approximately 30% of the exhaust flow is directed to a fabric filter to capture and remove particulate from the exhaust stream. Although most of the inorganic material is melted in GLASSPACK®, a small fraction of particulate can be carried over in the exhaust stream. The particulate is periodically removed from the filter bag media by pulsing the unit with pressurized air. Particulate removed from the fabric filter can be directed back into the process for conversion into glass aggregate.

After exiting the fabric filter, the exhaust is further cooled and water vapor, produced during combustion, is condensed in a packed tower condenser. The exhaust gas is cooled to 32 °C to 49° C (90° to 120° F) and directed into the gas recycle header where a portion of the exhaust gas, approximately 10%, is vented out of the process to advanced air quality control equipment as required by local air regulations.

The remaining 20% of the recycled gas is boosted in pressure through a recycle fan and enriched with oxygen. The end result is synthetic air which is injected back into Zone 1 of GLASSPACK®. Unlike normal air which is only 21% oxygen, synthetic air can be mixed to any ratio of oxygen necessary. This allows simultaneous optimization of melting temperatures, combustion conditions and emissions control not possible with conventional air fired combustion technology.

The GLASSPACK® closed-loop oxygen enhanced combustion process has instrumentation that is calibrated and functionally checked at start-up. The control system provides numerous interlocks which are intended to prevent the system from operating outside its normal design parameters. Both the oxygen supply system and the start-up natural gas supply system use double block valves, which are intended to isolate the energy supply to the melter in the event that any critical process parameter exceeds the limitations. Interlocks are also utilized that terminate granulate feed to the melter during abnormal conditions. Combustion ceases almost immediately upon trip because the melter system carries a very low inventory of granulate.

Heat Recovery

The heat energy recovered from GLASSPACK® can be transferred directly to a biosolids drying circuit. In most cases the dry biosolids provide enough thermal energy to eliminate the need for an additional energy source for drying. Figure 3 presents the supplemental energy requirements necessary to pre-dry biosolids of varying energy value and solids content. This figure illustrates that enough thermal energy can be recovered from GLASSPACK® to pre-dry biosolids from18% dewatered solids to 92% solids, if the energy content of the biosolids is > 18.5 MJ/kg (8000 Btu/lb), typical for undigested sludges. Similarly, no supplemental energy is required to pre-dry 13.9 MJ/kg (6000 Btu/lb) biosolids if the biosolids to be dried are dewatered to at least 22% solids, typical for digested sludges. Figure 4 illustrates this thermal energy balance for the GLASSPACK® process installed at the North Shore Sanitary District’s Sludge Recycling Facility, Zion, Illinois, USA.

Oxygen Supply

Oxygen consumption in GLASSPACK® is dependent on both the quantity of biosolids to be processed and their Gross Caloric Value (GCV). With US biosolids,

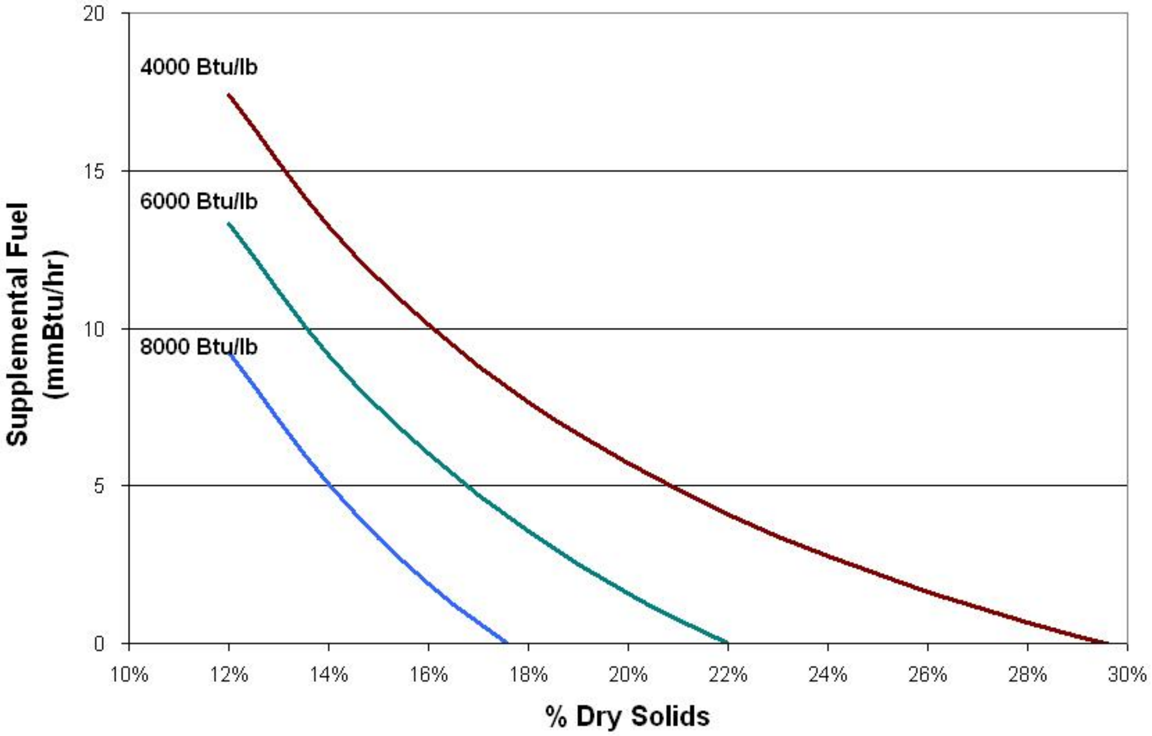


Figure 3. Supplemental energy requirements to dry sludge of various calorific values and moisture content to 92% dry solids.

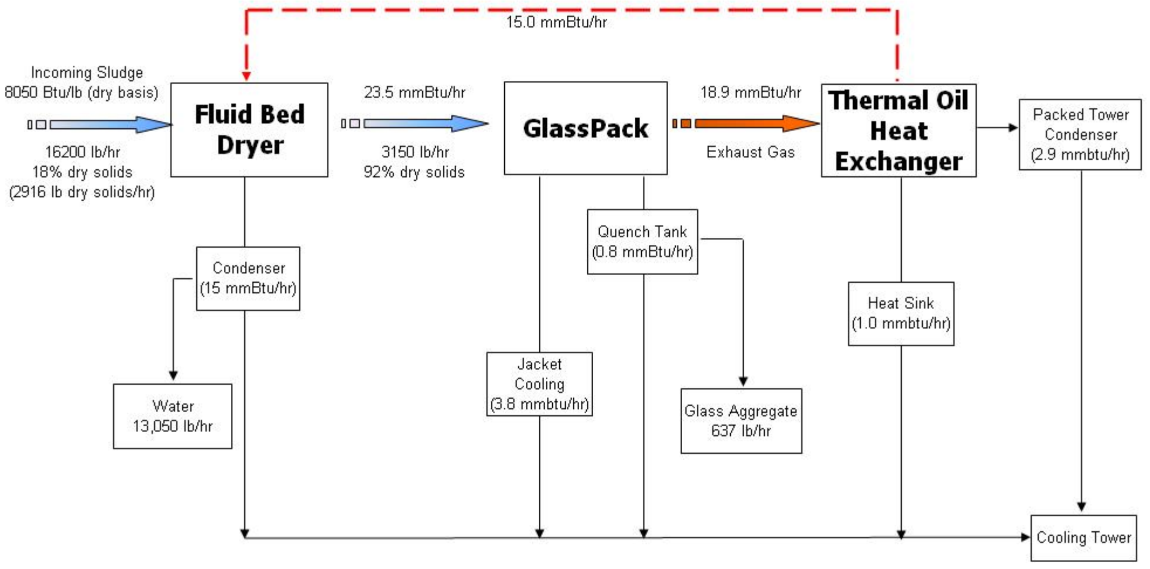


Figure 4. Mass and energy balance for GlassPack installation at North Shore Sanitary District Sludge Recycling Facility, Zion, Illinois, USA.

typically an average of 1.4 tons of oxygen are required for each dry ton of biosolids throughput, assuming a GCV of 18.5 MJ/kg (8000 Btu/lb). Lower caloric values will require less oxygen. Normal operation requirements for oxygen supply are >90% purity at 5 psig.

Oxygen can be provided to the process from either on-site liquid storage or generated on-site. Liquid oxygen (LOX) is normally 99% pure or higher, and the purity remains very constant. Liquid oxygen is produced at central production facilities and delivered to on-site storage tanks with special tanker trucks. Liquid oxygen is vaporized and warmed to ambient conditions to meet process demands. Liquid supply is most economical for small consumptions, less than 10 tons/day or when high purity (>95%) is required.

Oxygen can be generated on-site with either adsorption or cryogenic air separation technologies. Adsorption technology is most common at consumption rates between 10 and 150 tons/day and where purity of 90% to 95% is adequate. Cryogenic air separation provides the greatest range of production rates, up to 3000 tons/day and purity from 90% to 99+%. At consumption rates above 150 tons/day, cryogenic air separation is likely the best option.

Dry Granulate Feed System

Dried granulate from the dryer operation is conveyed to a roller mill with a volumetric feeder. The roller mill reduces the granulate size to the specified range, < 1 mm, for proper melter operation. The roller mill discharges to a granulate surge bin that supplies granulate to the melter through volumetric feeders. The volumetric feeders provide sized granulate to the melter through rotary airlocks.

GLASSPACK® Emissions

Emissions from GLASSPACK® are controlled through a combination of GLASSPACK® system configuration, GLASSPACK® process conditions, and commercially available technology (Table 1, Figure 2). With this combination, GLASSPACK® provides a level of emissions control that is unmatched by any other standard combustion technology and can meet the most stringent local, federal and EU criteria.

Eliminating ballast N_2 from the oxidizer source, Minergy's patented closed-loop oxygen enhance combustion, reduces stack volume and exhaust gas velocity as only oxygen necessary to sustain proper combustion is added. Exhaust stack volume is further reduced as the biosolids are pre-dried to >85% solids before being introduced into GLASSPACK®. Pre-drying the biosolids, in addition to being more thermally efficient, eliminates the vapor plume associated with evaporating large quantities of water in the combustion process. The combination of pre-drying biosolids and closed-loop oxygen enhanced combustion effectively reduces stack volume by > 92% when compared to standard combustion technology for an equivalent 100 dry ton/day operation (Figure 5).

Reduced stack volume increases residence time in GLASSPACK® resulting in more complete combustion and reduced formation of carbon monoxide, a product of incomplete combustion. Increased residence time and operating temperatures, necessary to melt the inorganic faction, increases destruction efficiency of volatile organic

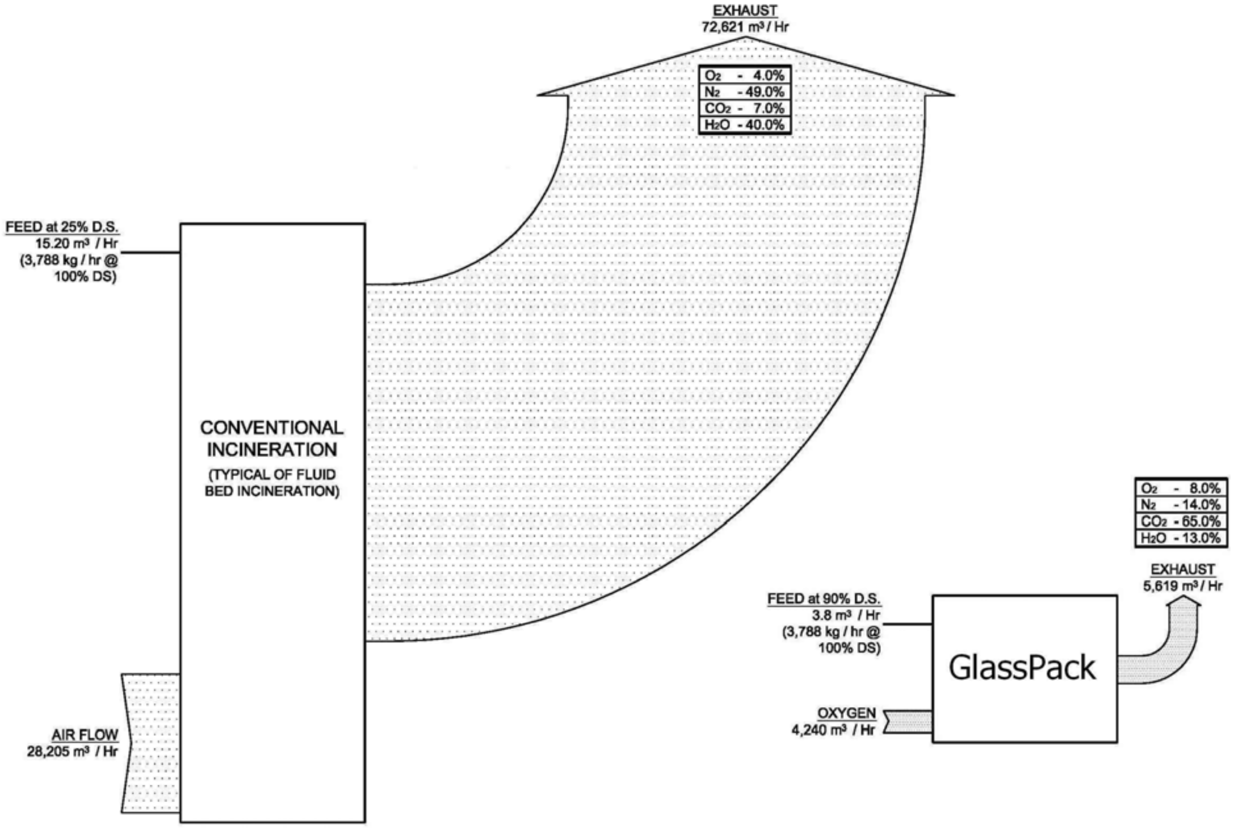


Figure 5. Vent flow comparison.

Table 1. Vitrification system component and control of emissions matrix.

GlassPack® System Component	Particulate Matter/Dust	NOx	Carbon Monoxide	Volatile Organic Compounds	SO_2/HCl/HF	Stack Volume
Pre-dry biosolids (> 85% dry solids)						✓
Closed-loop configuration		✓		✓		✓
Oxygen enhanced combustion	✓	✓	✓	✓		✓
Operating temperature > 2400^{o} F (>1300^{o} C)			✓	✓		
Fabric Filter (bag house)	✓					
Packed Tower Scrubber	✓				✓	
Additional NOx control on vent gases (if required)		✓				

compounds (VOC). Reduced gas velocity significantly reduces entrainment and carryover of biosolids particles while the operating temperature and residence time promotes glass formation (slagging) of the biosolids' inorganic fraction (Table 2).

Another benefit of the reduction in exhaust gas volume is that it can increase efficiency of flue gas treatment as pollutants are present in higher concentration and therefore easier to remove. Because GlassPack® intensifies the combustion process and reduces the volume of exhaust gases, the size of the air quality equipment will be proportionally reduced, reducing the required space, capital investment and operating and maintenance expenses.

In addition to emission benefits, closed-loop oxygen enhanced combustion provides significant process benefits including higher radiant heat energy, higher thermal transfer efficiency, improved ignition characteristics and greater flame stability. These process efficiencies lead to greater heat transfer to the biosolids and increased material processing rates through GlassPack®, further reducing overall emissions per ton of biosolids processed.

Table 2. Emission rate comparison between vitrification and conventional incineration technology

	Vent Flow(1) (lb/dry ton biosolids)		
	GlassPack®	Fluid Bed(2)	Multiple Hearth(2)
Particulate/Dust	0.60	460	100
NOx	2	2	5
Carbon Monoxide (CO)	0.2	2	31
Volatile Organic Compounds (VOC)	0.3	2	3

(1) Emissions assume no use of control technology
(2) Emission factors from US EPA AP-42

GLASS HIGH TEMPERATURE VISCOSITY

The composition of the inorganic fraction of the biosolids is critical to GlassPack® performance. Unlike substances such as metals that have a definitive melting point, biosolids do not. The minerals comprising the inorganic fraction of biosolids first soften and then gradually become more fluid over a large temperature range. Therefore, viscosity, a measure of a liquid's ability to flow (measured in poise), is an important property to understand when processing biosolids in GlassPack®.

In a melter performing vitrification, high temperature viscosity typically ranges from 10 to 250 poise. At a viscosity above 250 poise the material is too thick to flow unassisted and should be avoided in a melter. Proper and frequent mineral characterization of the biosolids is imperative to ensure a continuous flow of glass from the melter.

A common metric used to determine a material's high temperature viscosity property is T_{250}, the temperature at which the viscosity equals 250 poise. The T_{250} sets a lower limit of the GlassPack® operating temperature range. Ideally, in order to keep operating temperatures below 2800 ^{o} F the T_{250} should be <2350^{o} F. Operating temperatures above 2800 ^{o} F begin to compromise refractory life. It is normal to operate the melter above the T_{250} temperature; however, temperatures should be limited to prevent the glass viscosity from becoming to low. Glass viscosities less than 10 poise should also be avoided as the excess fluidity accelerates refractory corrosion rates.

A number of models have been developed to calculate the T_{250} from mineral chemistry. These models are only a guide to the material's high temperature viscosity property, as some mineral chemistries result in "unstable" glasses that no longer exhibit a temperature-viscosity relationship, but begin to exhibit a definite melting point. Many of these models do not properly account for the contribution of sodium (Na), phosphorus (P) and iron (Fe), often present in biosolids at significant concentrations, to the glass formation process. In general, many biosolids glasses indicate a T_{250} of 2350^{o} F or less (Table 3).

In situations where the T_{250} of the biosolids is unacceptably high, the composition can be manipulated to lower the melting temperature into the acceptable range. The T_{250} can be lowered through a process called fluxing, or the addition of specific substances that enable the material to fuse more readily. The addition of a flux material should be considered an alternative to high temperature operation. For example, Minergy's Fox Valley Glass Aggregate plant vitrifies up to 1300 tons of paper mill sludge a day that is extremely high in calcium (Ca). FVGAP fluxes the paper mill sludge with approximately 5% silica sand immediately before injection into the cyclone furnace to lower the T_{250} and maintain a steady glass flow.

Table 3. High temperature viscosity and mineral analysis

	T_{250}	**% Composition Ash Basis**										
Dry Granulate	**(^{o}F)**	**Al_2O_3**	**SiO_2**	**CaO**	**Fe_2O_3**	**TiO_2**	**Na_2O**	**MgO**	**P_20_5**	**K_2O**	**MnO**	**BaO**
New York, NY	2300	9.1	33.6	12.5	14.3	2.0	1.1	5.7	21.0	1.1	0.3	0.2
Pensacola, FL	2252	11.5	40.1	30.3	6.7	0.8	0.9	1.1	8.5	0.5	0.0	0.1
Mount Holly, NJ	2344	10.9	36.2	14.9	13.6	2.7	0.7	3.2	17.4	1.0	0.6	0.4
Milwaukee, WI	2306	8.4	33.7	8.9	22.2	1.0	1.4	5.0	18.5	2.7	0.1	0.1
Ocean County, NJ	2273	12.9	25.6	17.4	14.4	1.7	0.6	3.4	17.9	0.8	0.7	0.2
Detroit, MI	2550	20.8	46.5	9.2	8.0	0.8	0.7	3.6	4.9	2.4	0.1	0.1

Glass Aggregate

Markets for the glass aggregate product are large and diverse. More than 2.5 million tons per year of the material is currently produced in a similar industry known as slag marketing.

The process of water quenching the molten glass as it exists GlassPack® results in the formation of an environmentally inert aggregate (Table 4). During the quenching process, heavy metals that may be present are physically sequestered in the glass matrix resulting in very low leaching (Table 5).

Table 4. Physical properties of glass aggregated produced from vitrification of biosolids.

Physical Parameter	**Result**
> No. 4 sieve (ASTM C136)	24.4%
< No. 200 sieve (ASTM C136)	0.4%
Maximum Dry Density (ASTM D698-91)	108.5 lb/cf^3 at 13% moisture
Moisture Content (ASTM D2216)	2.2%
Organic Content (ASTM D2974)	<0.1%
Unit Weight As Received (ASTM C29/29M)	84.9 lb/cf^3
Specific Gravity (ASTM C127)	2.836
Soil Classification (ASTM D2487)	SP (Poorly graded sand with gravel)

Results from leach tests on glass aggregate produced from processing municipal biosolids meet criteria established by the Wisconsin Department of Natural Resources (WDNR) for Beneficial Reuse of Industrial Byproducts (NR538 Wis. Admin. Code). WDNR has granted Minergy two (2) Conditional Grant of Solid Waste Exemptions for glass aggregate produced from vitrification of high-volume industrial wastes. Minergy has also received Beneficial Use Determinations (BUD) from Illinois and Michigan regulatory agencies for use of glass aggregate produced from vitrification of biosolids. Approved uses identified in these exemptions and BUDs include roadbed construction, blended cements/pozzolan substitute, construction backfill, blasting media, roofing shingles and asphalt pavement.

One philosophy in beneficial reuse of glass aggregate produced from vitrification of high-volume industrial wastes is to concentrate marketing efforts on high volume applications. Obtaining and maintaining a small market share of multiple high-volume markets is easier than domination of one or two high value markets. Although these markets typically offer low return value, it is unlikely that entering into these markets will upset existing forces of supply and demand. Minergy's Fox Valley Glass Aggregate plant has been successful at beneficially reusing the glass aggregate produced from vitrification of paper mill sludge by pursuing high-volume low-value markets (Figure 7). For this reason, glass aggregate sales offsets should not typically be included in the economic analysis.

Table 5. Bulk chemistry analysis and TCLP extract analysis of glass aggregated produced by vitrification of biosolids from three major urban systems.

Parameter	New York City (April 2002)		City of Detroit (August 2000)		Milwaukee Milorganite (August 2005)	
	Bulk Analysis (mg/kg)	TCLP Extract (mg/l)	Bulk Analysis (mg/kg)	TCLP Extract (mg/l)	Bulk Analysis (mg/kg)	TCLP Extract (mg/l)
Aluminum	94000	0.028	51000	0.076		
Antimony	< 17	< 0.042	0.55	< 0.0014	< 9	< 0.0016
Arsenic	< 0.33	0.0013	9.1	< 0.0009	11	< 0.00061
Barium	1300	0.026	740	0.025	1400	0.00845
Beryllium	0.91	0.0025	0.8	< 0.001	2.7	< 7.5E-05
Boron	79	0.02	< 2.9	0.015		
Cadmium	0.14	0.00013	0.2	0.00038	5.6	0.00052
Chromium	210	0.0021	300	0.0027	0.26	0.011
Iron	60000	0.56	120000	2.9		
Lead	33	0.048	31	0.17	12	0.023
Manganese	1700	< 0.0018	870	0.15		
Mercury	< 0.042	0.0036	< 0.018	< 0.00018	0.063	0.00019
Nickel	100	0.0015	30	< 0.003	180	0.053
Selenium	< 0.44	< 0.0011	< 0.054	< 0.0012	4	0.00072
Silver	14	< 0.0001	1.3	< 0.00017	18	5.5E-05
Thallium	< 0.58	< 0.0014	< 0.03	< 0.0006	2.2	< 0.0015
Vanadium	150	< 0.002	260	0.0079	320	
Zinc	700	0.077	700	0.14	380	0.2