

ASH VITRIFICATION — A TECHNOLOGY READY FOR TRANSFER

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ABSTRACT

This paper discusses an aggregate manufacturing process developed by Marine Shale Processors, Inc. (MSP) which uses incinerator ash and baghouse dust from a hazardous materials recycling facility in the production of an environmentally safe vitrified slag. Environmental studies on the process feed stream and the aggregate product are summarized, as well as the operational characteristics of the vitrification process. Results of a heavy metal leaching study are also reported.

INTRODUCTION

Marine Shale Processors, Inc. (MSP) is continuing a research program aimed at producing an inert, safe aggregate from combustion by-products. This paper briefly reviews the problems associated with combustion ash disposal, the advantages of vitrification, and results of a laboratory investigation into the physical and leaching characteristics of vitrified ash. The MSP aggregate manufacturing process is described, as well as a proposed method for using vitrification in the treatment of ashes from other facilities.

CURRENT ASH MANAGEMENT PROBLEMS AND POSSIBLE SOLUTIONS

Most of the problems associated with ash management can be traced to the lack of definition or regulatory direction from government agencies. Technical answers, regulatory initiation, court orders, legislative actions, or a combination of these activities will be used to resolve the questions surrounding the combustion ash issues [1]. In whatever actions are taken, technical solutions which incorporate reuse/recycle will be preferred alternatives to disposal in landfills. The safe reuse/recycling of combustion ashes into products such as construction materials will allow us to make better management decisions in the overall waste disposal dilemma.

EPA has initiated a program which is evaluating technologies to stabilize, or reuse incinerator ash [2]. In addition, there are many investigations related to ash management which promote reuse/recycle as viable alternatives [3-8]. Most of the data presented in these papers suggest that incinerator ash may contain small amounts of organic compounds and various metals, depending on the materials burned. Methods of treatment range from landfilling, and various methods of solidification, to thermal treatments such as vitrification.

In the recent past, fly ash has been used extensively in the production of concrete and cement [11]. Bottom

ash and slagged materials are suitable materials for use in subgrade applications. In the 1950s and 1960s, several federal agencies endorsed the use of ashes in large construction projects, and in the 1976 RCRA legislation, agencies were directed to use fly ash in concrete applications as often as possible [11].

Tests have been carried out in Europe where fly ash was made inert through a slagging process and the product used in road construction, or safely used in other ways. Slagged material has also been used extensively for road construction in the United States.

Several cases relative to ash toxicity as measured by the EP tox test are in court, and should prompt congressional decisions regarding methods for treating ash in the near future [1]. The lack of specific rules by RCRA has led to confusion and general disposal practices for ash based on its being a nonhazardous waste. Whether or not an ash is hazardous or non-hazardous depends largely on results obtained from the EPA's EP toxicity tests for heavy metals, another controversial issue. These tests have shown that lead and cadmium are the two metals occurring in concentrations high enough to consider the ash sampled to be toxic. Results also show that the EP toxicity test reproducibility is poor, procedures are ill defined, and it appears that a bias exists from one testing laboratory to another. Yet, this is the best (or only) test available and results from testing ash have prompted some investigators to propose the "upfront delisting" of incinerator ash [9].

Congress is considering several bills which, if enacted, would eliminate the use of the EP toxicity test and would direct the EPA to develop regulations for the disposal of ash [10].

Further refinement of fly ash and bottom ash by a sintering or vitrification process has proven to be an acceptable practice in producing light weight aggregates which are suitable for use in construction projects. The balance of this paper is directed to vitrification as a primary choice, and specifically to the vitrification process developed by Marine Shale Processors, Inc.

VITRIFICATION

Vitrification is a process wherein materials such as silica, silica oxides, or iron oxides are changed into a glass-like substance. DOE laboratories have been doing vitrification research for many years in programs designed to treat radioactive materials [13]. They have shown the vitrifying process to be an excellent method for reducing the volume of irradiated wastes and a

good storage method. Recently, these research efforts have been directed to the treatment of waste materials from combustion processes, and specifically to hazardous waste combustion processes. These researchers find that molten glass can dissolve, or capture, most inorganic materials and when cooled to a solid state, it is highly resistant to groundwater leaching. Various forms of glass are predictably stable, and therefore, an excellent medium for encapsulating hazardous materials.

PROCESS DESCRIPTION

MSP recycles hazardous and industrial solid materials as raw ingredients to produce usable aggregate (See Fig. 1). The primary elements of the processing system are a 275 ft (83.82m) counter-current rotary kiln, a puddling furnace, two oxidizers, a dry spray reactor, and baghouses for particulate control. Sludges and solids, including shredded containers, are blended to generate a material having a heat content between 8000–11,000 Btu/lb (18,600–25,570 J/g). Raw ingredients are fed into the elevated end of the kiln and move toward the lower end with a residence time of 120–150 min. The lower end of the kiln is fired with natural gas and liquid fuels. Oxygen and makeup air are also introduced at the lower end to support oxidation and maintain temperatures at approximately 2192°F (1200°C). Solids exiting the lower end of the kiln are separated, with fine materials sent to be vitrified in the puddling furnace at the transition between Oxidizers A and B. Large materials (gravels) are stored for testing before sales, as are ferrous materials.

Gases travel up the kiln and enter the oxidizers where virtually all remaining organic materials are destroyed at temperatures ranging from 1600°F to 2300°F (870°C to 1260°C). Residence time in the oxidizers is about 7 sec.

About two-thirds of Oxidizer C is a dry spray reactor for neutralization of hydrogen chloride (HCl) and other acidic species. The process gases exit the dry spray reactor at approximately 350°F (175°C) and consist of about 60% water vapor by volume. Particulates are removed from the vent stream by baghouses. After going through dual induced draft fans, gases are vented to the atmosphere at the rate of 160,000 ft³/min (4530 m³/min) at a temperature of 325°F (163°C).

VITRIFICATION

Figure 2 is a schematic diagram of the MSP vitrification process. The primary source of energy for melt-

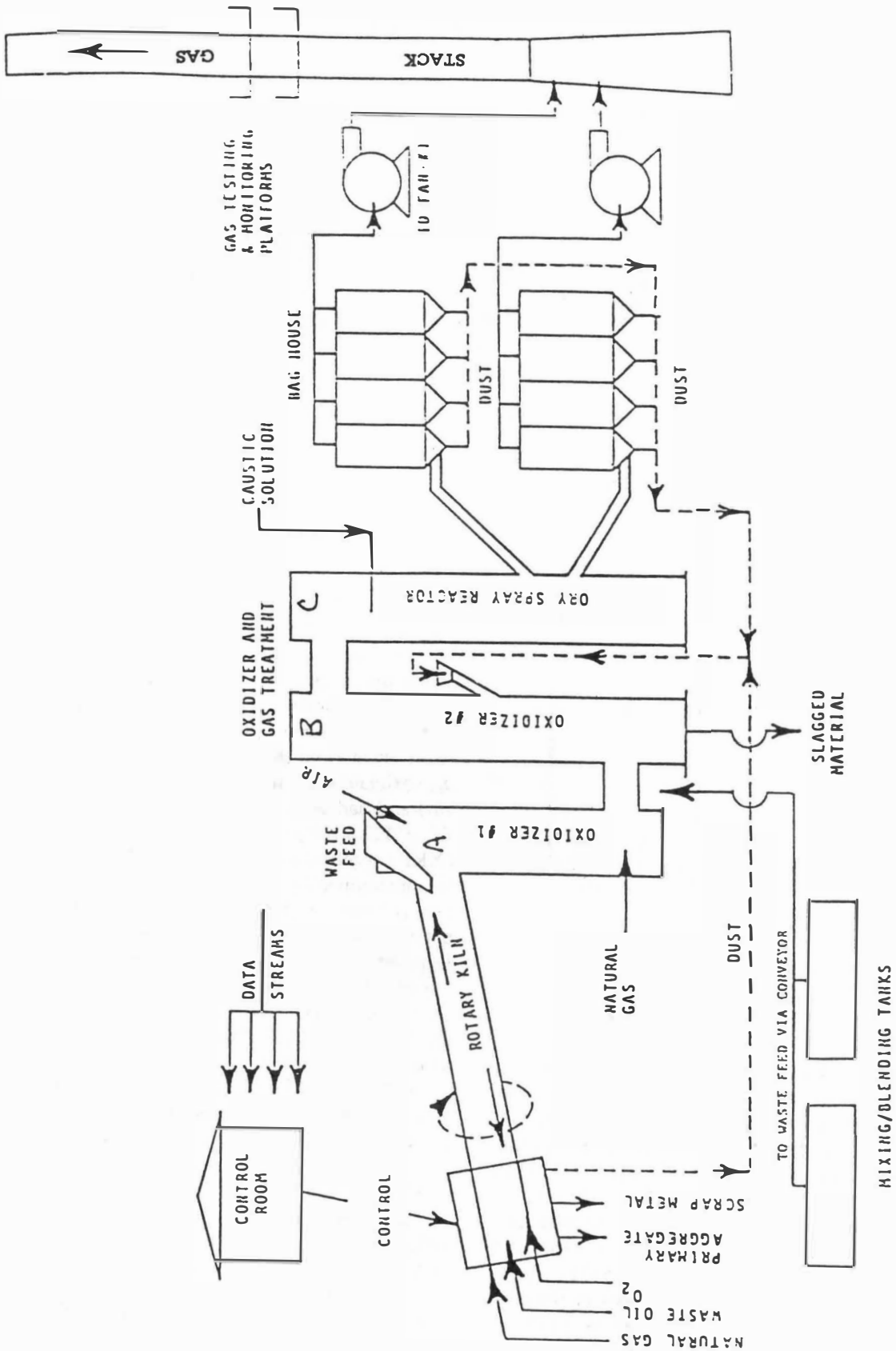


FIG. 1 SIMPLIFIED SYSTEM SCHEMATIC

TABLE 1 MSP SLAG ANALYSIS

Constituent	Typical MSP Slag (weight %) Range			Typical Blast Furnace Slag ⁽¹⁾ (weight %) Range		
Al ₂ O ₃	5.40	-	6.10	8	-	17
SiO ₂	25.00	-	33.00	32	-	40
Cl	0.17	-	0.44	N/A	-	N/A
CaO	7.90	-	11.00	32	-	44
Cr ₂ O ₃	0.60	-	0.66	N/A	-	N/A
MnO	0.30	-	0.31	0.2	-	0.8
Fe ₂ O ₃ (2)	29.00	-	38.00	0.1	-	1.5
CuO	0.58	-	0.79	N/A	-	N/A
ZnO	1.90	-	2.40	N/A	-	N/A
Br ₂ O ₅	0.07	-	0.142	N/A	-	N/A
BaO	14.00	-	16.00	N/A	-	N/A
PbO	0.26	-	0.32	N/A	-	N/A
Sr ₂ O ₃	0.30	-	1.31	N/A	-	N/A
MgO	ND	-	ND	2	-	19
S	N/A	-	N/A	0.6	-	2.3

- (1) Industrial Minerals and Rocks Handbook
- (2) ONLY Fe₂O₃ (hematite) was identified s crystalline material.
- ND Not Deleted
- N/A Not Available

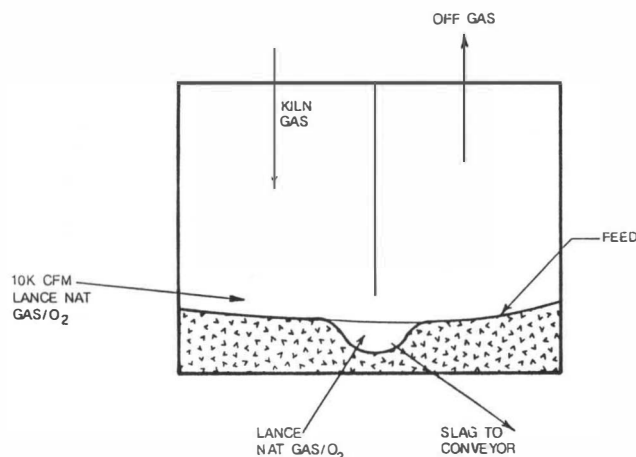


FIG. 2 SLAGGING SECTION OF OXIDIZER VESSELS

ing the process residue is the gases from the combustion process. This is augmented with a natural gas/oxygen lance which is located so that the flame impinges on the molten surface. By-products are fed to the smelting section, and the lava migrates to the lower section of the smelter where it enters a pooling pot. Here, a second lance is used to maintain a constant fluid level and smoothly flowing molten stream which pours into the water-cooled screw conveyor. The size of aggregate pellets is controlled by varying the speed of the conveyor. In normal operation, the MSP process produces approximately 100 tons/day of aggregate. Table 1

shows the results of laboratory analysis on the MSP slag and Table 2 presents the results of leaching tests on the slagged material.

The data presented in Table 2 was derived from the Toxic Characterization Leaching Procedure (TCLP) extraction tests conducted on slag samples which were relatively fine graded. The materials ranged in size from approximately 0.2 in. (0.508 cm) to 0.02 in. (0.0508 cm) and had an average unit weight of about 70 lb/ft³ (0.112 g/cc). Analysis using x-ray fluorescence (XRF) spectrometry and x-ray diffraction show that the predominant crystalline constituent in these samples is hematite (Fe₂O₃) [15]. Data in Table 3 was obtained from slag samples tested by the Louisiana Department of Environmental Quality (DEQ) [16].

From February 15 to 18, 1989, Woodward-Clyde Consultants (WCC) conducted a sampling program at the MSP plant [17]. Hourly samples of the raw ingredient feed material, fuel oil, and the aggregate produced from this feed and fuel oil were collected for laboratory analysis. Samples were collected over an 8 hr period to account for the lag time between the time raw materials enter the process as feed and exit as finished aggregate.

The purpose of this program was to evaluate the effectiveness of the MSP aggregate manufacturing technology in terms of environmental factors by analyzing and comparing environmental characteristics of the materials entering the process with those of the finished aggregate product. Table 4 summarizes the hazardous

TABLE 2 MSP SLAG AGGREGATE QUALITY REPORT

MONTH: JANUARY, 1989 ANALYSIS: TCLP METALS								
DATE	ARSENIC	MERCURY	SELENIUM	CHROMIUM	CADMIUM	LEAD	BARIUM	SILVER
3	0.1		0.06		0.03	0.86	1.05	0.04
4			0.06		0.03	0.61	1.39	
5	0.07		0.02			0.03	3.71	
6	0.02		0.05		0.01	0.82	0.66	
7	0.1					0.17	0.66	
8	0.64		0.45	0.03	0.03	0.45	1.79	
10	0.18		0.07		0.02	0.3	0.51	
11	0.14		0.11		0.02	0.41	0.45	
12	0.14		0.09		0.01	0.26	0.3	
13	0.32		0.23		0.02	0.22	0.37	0.04
14						0.17	0.48	
15	0.07		0.05	0.01	0.01	0.14	0.31	
17	0.06		0.02			0.07	0.27	
18			0.01			0.15	0.2	
19	0.04		0.02			0.08	0.34	
20	0.07					0.05	0.29	
21	0.05		0.01	0.01		0.05	0.18	
22	0.01					0.12	0.28	
24			0.03		0.01	0.07	0.28	
25	0.02					0.08	0.52	
26	0.06					0.18	0.41	
27	0.12		0.06			0.08	0.42	
28	0.08		0.02		0.01	0.09	0.72	
29	0.04		0.02			0.04	0.32	
30	0.05					0.04	0.27	
31	0.02		0.04			0.05	0.29	
MONTHLY AVERAGE	0.109	<D.L.	0.075	0.017	0.015	0.215	0.633	0.040
STANDARD DEVIATION	0.134		0.101	0.009	0.010	0.228	0.717	0.000

1. ALL CONCENTRATIONS ARE IN MILLIGRAMS PER LITER.
2. THE BLANK ENTRIES REPRESENT THE CONCENTRATIONS ARE BELOW THE DETECTION LIMITS.

TABLE 3 LEACHATE ANALYSIS — MSP SLAG

Test	Concentration (mg/l) in TCLP Extract	TCLP Limits	MOL (mg/l)
Arsenic	BQL *	5.0	0.002
Barium	0.8	100.0	0.1
Cadmium	0.010	1.0	0.005
Chromium	BQL	5.0	0.05
Lead	0.43	5.0	0.05
Mercury	0.0007	0.2	0.0002
Selenium	BQL	1.0	0.002
Silver	0.01	5.0	0.01

Test	Concentration (mg/l) in TCLP Extract	TCLP Limits	MOL (mg/l)
Arsenic	BQL	5.0	0.002
Barium	0.6	100.0	0.1
Cadmium	0.027	1.0	0.005
Chromium	BQL	5.0	0.05
Lead	0.19	5.0	0.05
Mercury	0.0014	0.2	0.0002
Selenium	BQL	1.0	0.002
Silver	0.01	5.0	0.01

* BQL — below quantification limits.

compounds identified, their concentrations and the total amount of these compounds in the input streams. The total amount of hazardous compounds in the feed and in fuel oil is only a small fraction of the total material input.

Nineteen priority pollutant organic compounds were found in the feed, and fifteen were found in the fuel oil. None, however, were found in the aggregate product which suggests that volatile organic compounds are reduced to their constituent elements by the process and are not retained in the finished aggregate.

The TCLP was utilized to extract leachable toxic metals (the eight listed TCLP metals plus nickel and thallium) from the samples. None of these metals exceed the EPA hazardous waste characteristics limits (proposed in the June 13, 1986 Federal Register) in the aggregate leachate. This substantiates the results of the DEQ tests (Table 3).

The TCLP metal concentrations in the leachate of all the samples tested are summarized on Table 5. Based on these results it appears that the MSP process effectively binds metals in the aggregate matrix to re-

TABLE 4 QUANTIFIABLE ORGANIC PRIORITY POLLUTANTS AND LAND BAN COMPOUNDS ¹ (mg/kg)

CONSTITUENT	FEED	FUEL OIL	DETECTED IN AGGREGATE
Butyl Benzyl Phthalate	218.	575.	0
Di-N-Octyl Phthalate	88.0	-	0
Hexachloroethane	249.	-	0
Naphthalene	404.	853.	0
Isophorene	84.	-	0
1,2,4 Trichlorobenzene	152.	-	0
1,2 Dichlorobenzene	-	486.	0
Phenol	1180.	3260.	0
1,1,2,2 Tetrachloroethane	-	102.	0
Benzene	-	12.9	0
Carbon Tetrachloride	-	5.3	0
Chloroform	14.9	443.	0
Dichloroethane	29.	-	0
Ethylbenzene	56.	105.	0
Methylene Chloride	1570.	2080.	0
Tetrachloroethene	104.0	174.	0
Toluene	1230.	1370.	0
1,1,1 Trichloroethane	204.0	756.	0
Trichlorofluoromethane	13.5	-	0
Total Xylene	332.	563.	0
Trichloroethene	164.	375.	0
Acetone	63.	-	0
Methyl Ethyl Ketone	259.	-	0
Methyl Isobutyl Ketone	240.	734.	0
Chlordane	620.0	-	0
Gamma-BHC	40.0	-	0
Total in mg/kg	7314.4	11894.2	
Total in Percentage	0.73%	1.189%	

¹From August 17, 1988 Federal Register

duce their leachability by as much as three orders of magnitude when compared to the input materials.

TECHNOLOGY TRANSFER

Vitrification is a method for producing an acceptable, safe product, and there needs to be an effort dedicated to promoting this technology to all potential users. For instance, consider the operations of a Massachusetts Refuse Derived Fuel (RDF) facility producing 120 tons of bottom ash per day [11, 12]. After separating nonferrous metals, ferrous metal and oversized material, this plant produces a net 112 tons of valuable material, referred to as "boiler aggregate," which is used in the fabrication of concrete. Concrete blocks made from this ash never showed EP tox results in excess of regulatory limits when tested, even when crushed to sizes smaller than 9.5 mm. This suggests that the metals in the ash are chemically immobilized, as well as being physically encapsulated. Vitrification of ashes, and their use in construction materials such

TABLE 5 CONCENTRATION OF TRACE METALS IN LEACHATE (mg/L)

Parameter	Feed	Fuel Oil	Aggregate	TCLP Limit ¹
Arsenic	0.0175	0.04	<0.01	5.0
Barium	0.825	0.1	0.175	100.0
Cadmium	14.8	0.64	0.015	1.0
Chromium	0.575	0.42	0.825	5.0
Lead	43.75	0.3	0.15	5.0
Mercury	0.005	0.005	0.00035	0.2
Selenium	0.04	0.01	<0.01	1.0
Silver	0.0525	0.01	0.01	5.0
Nickel	0.455	0.78	0.065	--
Thallium	<0.1	<0.01	<0.1	--

Note: Feed and Aggregate values are an average of the 4 daily composite samples.

¹From 6/13/86 Federal Register

as concrete/asphalt should accomplish the same end, probably to a greater degree of safe encapsulation.

The MSP example of technology transfer is relatively straightforward. All one needs is a source of heat and a control mechanism. Feeding rates, temperature and quenching rate are important control points; lava flow geometry, and method of ash feed are also important considerations. Figure 3 is a typical municipal waste combustor (MWC) schematic, modified to include a vitrification section which replaces the usual ash disposal method—landfilling. Here, the hot combustion gases from the secondary combustor are used as a primary heating source for the raw ingredients. Ashes are segregated (ferrous and nonferrous metals, and oversized grains) at the ash discharge point. The residue is recycled to the melting chamber. Additional energy sources (gas lances, or electrodes) are used to obtain the desired temperature and to maintain molten flow. Air or water can be used to cool the slag, depending on the desired slag properties. If the MWC facility is producing electrical energy, it would be advantageous to use electrodes as the energy control sources [18]. The placement and position of the electrodes will depend on the flow properties (depth, speed, etc.) of the molten slag, and the rate of ash feed. Process heat recovery (hot air or steam at > 1000°C) can be used to preheat the ash bed. Natural gas/air lances could then be used to control the molten state and flow rate.

These suggestions are not necessarily new. The technology is available, and there is a pressing need to promote the thermal treatment of MWC and other ashes. In 1990, the new land ban regulations will require ash treatment—vitrification is a viable option.

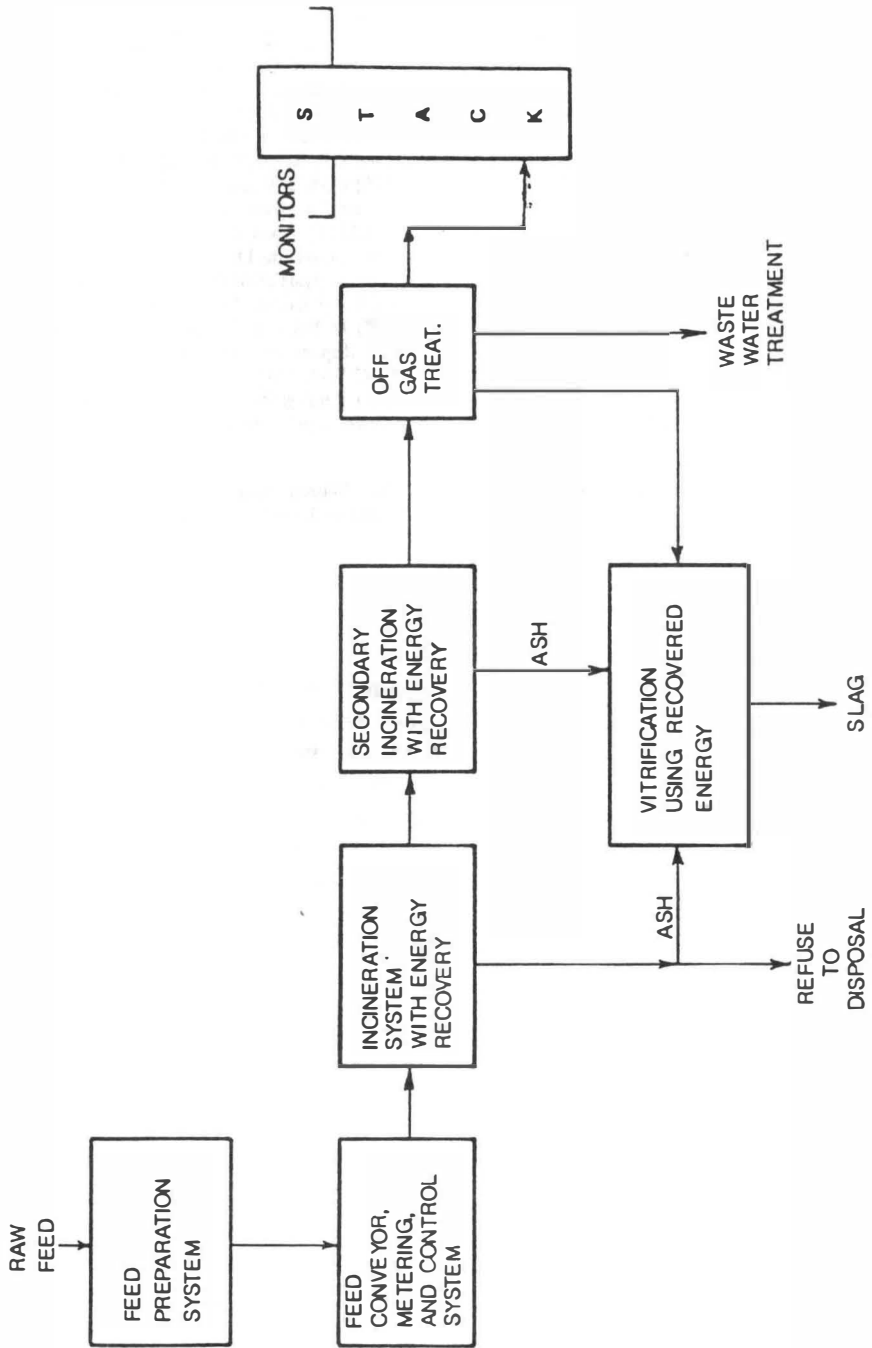


FIG. 3 MODIFIED MWC SYSTEM BLOCK DIAGRAM

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Key Words: Ash; Fly Ash; Glass; Heavy Metals; Incineration; Leachate; Vitrification