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Beneficial Recycling of Metal Refining Wastes via Gasification

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Presented at
Gasification Technologies 2001
San Francisco, California
October 7 – 10, 2001

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ABSTRACT

The processing of various feed streams in modern slagging gasifiers, and the conversion of the contained carbon portion into the commodity known as Synthesis Gas has been known and practiced commercially for a significant period of time. As this technology has developed, the economic and environmental benefits of gasification become more and more apparent. Successful gasification of coals, high sulfur Petroleum Coke, Bio Mass Solids, Municipal Solid Wastes, and Liquid Industrial Wastes have been demonstrated. As more Research and Development is conducted into the various gasification technologies, the superior environmental performance of gasification over older, alternative technologies such as landfill, incineration, etc are becoming increasingly obvious. For example, the gasification of even highly chlorinated organic compounds does not result in the formation of polychlorinated dioxins and furans, unlike incineration, which generates a considerable quantity of these toxic by-products. This paper will describe the preliminary results of a program to extend the utility of modern slagging gasification to the beneficial recycling of Spent Aluminum Potliner – a unique waste characterized by the presence of cyanides, arsenic, polyaromatic hydrocarbons, and a significant concentration of fluoride.

INTRODUCTION

The use of gasification for the production of high quality Synthesis Gas for a variety of applications has increased dramatically during the last several years. It has been estimated[1] that over 58,000 MW Thermal (equivalent to over 32,000 MWe IGCC capacity) of Synthesis Gas projects currently are active or planned worldwide. These projects span the application range and include electric power production, steam production, hydrogen manufacture, fuel cells, and chemical manufacture of such products as ammonia, methanol, oxochemicals, Fischer-Tropsch fuels, acetyls, acetic acid, and acetic anhydride.

Initially, gasification was developed primarily for the conversion of coal to Synthesis Gas, but in recent years increased attention has focused on the gasification of petroleum coke. Petroleum coke represents the last, and least desirable, portion of a barrel of petroleum crude after all the lighter components have been captured. Such material can contain as much as seven (7) percent of sulfur or more, making it difficult to utilize in most applications. It has been demonstrated conclusively by Global Energy, Inc.[2] (and others) that such high sulfur Petroleum Coke may be gasified utilizing its E-GAS™ Gasification Process to form a Synthesis Gas with characteristics similar to the Synthesis Gas produced from typical coals, which contain significantly less sulfur. In fact, operation on petroleum coke with a sulfur content of 5.7 % has produced a Synthesis Gas with almost identical composition to that produced from coal with a much lower sulfur content. This represents a sulfur removal efficiency of greater than 99 %. In addition, operation of the gasification equipment was smooth and efficient. Use of this powerful gasification technology makes the Wabash River Energy facility the cleanest coal or coke fired power plant in the world, with overall SO_x emissions less than one tenth of Clean Air Act standards and with no detectable particulate emissions. This information base will allow Global Energy to design a new generation of E-GAS™ gasification facilities that meet the technological needs of the marketplace, the economic needs based on the current raw material supply costs, and the environmental needs of the nation.

Increasingly, investigators are examining gasification as a cost effective solution for dealing with various carbon-containing waste streams. Waste minimization and waste recycling strategies of the EPA and other regulatory agencies clearly are impacted positively. The conversion of carbon- or organic-bearing constituents to a Synthesis Gas, sulfur to elemental sulfur, and the inorganic constituents to vitreous frit, all of which are value added products, fit into EPA's stated strategies for waste handling and treatment. A permit for the gasification of municipal solid waste/coal briquettes in a BGL gasifier has recently been issued to Global Energy for their Kentucky Pioneer Energy project.[3] This project is permitted to feed up to 190,000 Kg/hr of a 60/40 mixture of municipal solid waste and coal to produce Synthesis Gas, which in turn will be used to power two GE 7FA gas turbines, producing 540 MW (net) of electric power. In the area of industrial waste streams, Dow Chemical Company[4] has reported on a process to gasify highly chlorinated waste streams derived from their chlor-alkali/ethylene derived product manufacture. In this process, not only are the carbon and hydrogen components recovered for recycle (as a Synthesis Gas), but also the chlorine will be recycled as either aqueous or anhydrous hydrogen chloride. The gasification of nitrogen-bearing industrial waste materials derived from various nylon manufacturing processes also has been demonstrated.[5] These waste materials can contain up to 24 percent by weight of carbon-bound nitrogen. Traditionally, incineration of these materials was the primary disposal method, resulting in significant concentrations of NO_x being produced. In contrast, in the gasification process, organic-bound nitrogen primarily is converted to diatomic nitrogen under the reducing conditions present in the gasifier, therefore, representing a distinct environmental advantage.

Initially, with new and innovative waste treatment technologies, the questions regarding the fate of principal organic hazardous constituents (POHCs), the possible production of chlorinated dioxins and furans, or the production of products of incomplete combustions (PICs) which are commonly associated with incineration based technologies always are of concern. Extensive studies of gasification processes[6, 7] have shown that such concerns are unfounded. Studies on the gasification of hexachlorobenzene and polychlorinated biphenyls[8] have shown exceptional destruction efficiencies and essentially background levels of 2,3,7,8-tetrachloro-dibenzodioxins which are orders of magnitude lower than the commonly accepted *de minimus* risk limit of 1.0 nanogram per cubic meter. This is in spite of the fact that the molecular structures of the chlorinated benzenes and biphenyls are set up spatially for the direct formation of dioxins and furans, a reaction that does not occur in the reducing atmosphere within the gasifier. Even the presence of large quantities of organic chloride, as in the Dow study,[4] did not result in even *de minimus* production of dioxins or furans.

With the exceptional environmental performance of gasification systems so well documented, EPA currently is in the process of addressing whether secondary refinery wastes from the petroleum industry and the derived Synthesis Gas may be excluded from the definition of solid waste if they are gasified in a modern slagging gasification process.[9] In addition, EPA also is assessing whether such exclusion may be extended to include other RCRA wastes from other industries.[10] The purpose of this paper is to present preliminary results from studies on the gasification of waste materials derived from the metals refining industry – specifically the gasification of Spent Aluminum Potliner. The results from this study clearly show the robust nature and tremendous flexibility of slagging gasification, even when applied to a rather exotic type of waste stream such as Spent Aluminum Potliner.

THE ALUMINUM INDUSTRY / SPENT ALUMINUM POTLINER

Spent Aluminum Potliner (SPL) is a listed hazardous waste (designated K088) derived from the aluminum smelting process known as the Hall-Heroult process.[11] Prior to the invention of this process in 1886, aluminum metal was quite rare and expensive. The Hall-Heroult electrolytic process for the production of aluminum changed all that, giving birth to this huge industry segment. The aluminum production takes place in large metal cells called aluminum pots. The metal cell first is lined with refractory brick (alumina and silica), which in turn is lined with conductive carbon to form the cathode of the cell. A molten mixture of cryolite (Na_3AlF_6) and aluminum fluoride (AlF_3) at a temperature of about 950^0 Celsius is placed within the cell to act as an electrolyte. A carbon anode is used to complete the circuit. Aluminum oxide (Al_2O_3) is added to the electrolyte and an electric current is passed through the cell. Molten aluminum migrates and forms at the cathode while oxygen migrates to the anode. The molten, purified aluminum is withdrawn and cast into ingots destined for various manufacturing uses. A schematic of a typical cell is shown below in Figure I:

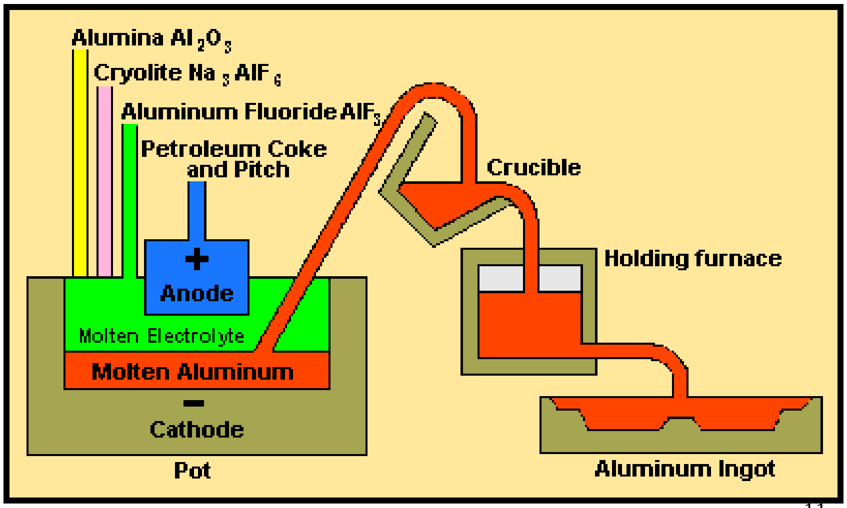

Figure I: Schematic of a Typical Aluminum Electrolytic Cell[11]

Considering the high temperatures involved as well as the nature of the molten salt bath, it is not unexpected that the refractory and cathode linings of the cell break down over a period of time. Eventually, the cell no longer operates acceptably and must be taken out of production. At this point, the refractory and cathode lining are removed from the pot in pieces ranging in size from relatively large blocks down to dust. This Spent Aluminum Potliner material then is classified as a waste material – Hazardous Waste Classification K088. EPA estimates that a large volume of SPL on the order of 100,000 – 125,000 tons per annum is generated in the United States alone.[12] Approximately half that annual volume with an additional stored volume of greater than 500,000 tons is generated or available from the Canadian market as well.

The SPL may be classified as one of two “cuts” – one containing predominately refractory material and the other containing mostly carbon cathode material. For the purpose of this study, however, a mixture of both cuts obtained from a German aluminum manufacturer was used. Analysis of the SPL material can be seen in Table I. Note that the carbon contents of the individual cuts can range from approaching zero to 60 percent. The heating value of the material mixture used in this test program is equivalent to approximately 4,030 BTU per pound. This is a relatively low heating value but still is considered sufficient to maintain the requisite temperatures for the gasification reactions within the gasifier.

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Table I
Analysis of Spent Aluminum Potliner
(in weight percent unless otherwise noted)

Proximate Analysis:		**Ash Analysis:**	
Moisture	0.6	SiO_2	13.6
Ash	71.0	Al_2O_3	39.9
Volatiles	4.1	Fe_2O_3	2.8
Solids	95.3	CaO	2.6
Fixed Carbon	24.3	MgO	0.4
		SO_3	0.5
Ultimate Analysis:		TiO_2	0.4
Carbon	26.2	P_2O_5	<0.1
Hydrogen	0.3	Cr_2O_3	<0.1
Oxygen	1.2	MnO	<0.1
Nitrogen	0.6	V_2O_5	<0.1
Sulfur	0.3	Na_2O	26.6
Fluorine	16.7	K_2O	0.8
Cyanides (mg/kg)	146.0		
Arsenic (mg/kg)	8.0	**Heating Value:**	
		HHV (kJ/kg)	9360
		LHV (kJ/kg)	9290
		Melting Point: deg C.	1520

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The SPL constituents of concern to the EPA include cyanide (which may be present at elevated levels of between 0.1 – 1.0 percent), toxic metals (especially arsenic) and leachable fluoride. In addition, polycyclic aromatic hydrocarbons (PAHs) also present some concern. The SPL used in this investigation contain a moderate level of cyanides at 146 mg/kg. Although lower than the maximum elevated levels of cyanides observable, this level is sufficient to test the efficacy of the gasification technology for treating this type of constituent. The arsenic level of only 8.0 ppm is low, however, arsenic usually is not a major constituent of SP. The EPA's concern relative to arsenic is the result of the arsenic levels generated in the treatment of K088 by one of the alternative treatment technologies. The significant fluorine content (16.7 percent) is at the general upper end of the range of fluorine and represents an excellent test case for studying the utility of gasification technology as a treatment technology for Spent Aluminum Potliner.

ALTERNATE TECHNOLOGIES FOR SPL TREATMENT

There are two alternate technologies currently in use for treating Spent Aluminum Potliner. Reynolds Aluminum developed the first of these technologies at a treatment facility located in Gum Springs, Arkansas[13]. This facility is reported to have a capacity of roughly 120,000 tons/annum. In this process, SPL is first ground or otherwise properly sized, mixed with roughly equal portions of limestone and brown sand, fed to a rotary kiln, and heated. The mixing and heating process was designed to thermally destroy the PAHs and cyanide, while limiting the leachability of the fluoride through creation of calcium fluoride, which is considered to be insoluble. The process, however, creates a residue approximately 2.5 times greater by weight than the original quantity of K088 treated. This residue was able to pass the then mandated treatment standards (See Table II) for non-wastewater forms of K088, which included the Toxic Characteristics Leaching Profile (TCLP).

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Table II
Selected Treatment Standards for K088

Component	Non-wastewaters	Wastewaters
Fluoride	NA	35 mg/L
Cyanide (total)	590 mg/kg	1.2 mg/L
Arsenic	26.1 mg/kg	1.4 mg/L

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The Reynolds residue then was placed into a dedicated monofill landfill at Gum Springs as well as into unlined pits at a Hurricane Creek, Arkansas mining site. It was later determined that significant levels of cyanide (46.5 mg/L), arsenic (6.55 mg/L) and fluoride (2228 mg/L) were present in the leachate from the monofill, with lower (but still significant) levels observed at the Hurricane Creek site. EPA stated, "that the increased mobility of cyanide, fluoride, and arsenic are due to the highly alkaline conditions that exist at Reynolds' Gum springs monofill." [13] Such high alkalinity is due largely to the unique characteristics of the Gum Springs residue, which pass the acidic-pH leachate test of the TCLP. The apparent inability of this technology to stop the leaching of toxic constituents under highly alkaline conditions led to the search for alternate technologies.

Ormet Corporation offers the second technology alternate under a license from Vortec Corporation. This technology is based on vitrification in which the finely crushed SPL and other glass making constituents (sand and limestone) and are mixed together and melted, or vitrified, to form a glassy frit. [14] This is accomplished in a process that includes a counter rotating vortex reactor, a cyclone melter, and a separator. Natural gas and preheated air are utilized to obtain temperatures of 2400^0 Fahrenheit. The carbon containing components of the SPL (including any cyanide constituents) are combusted completely with air to form carbon dioxide. The fluoride components are volatilized, exit with the off gases and removed separately as “baghouse dust”. Any arsenic that is present in the SPL would be volatilized along with the fluoride components and end up in the “baghouse dust”. Remaining inorganic components of the feed materials would be incorporated into the glassy frit residue, which contains fluoride at a low level of approximately 38.5 mg/kg. Studies have shown that this glassy frit exhibits very low leaching characteristics – especially fluoride, cyanide, and arsenic. The majority of the fluoride and arsenic contents of the SPL wind up in the baghouse dust, however.

The fluoride levels of the baghouse dust would limit the application of this material to reclamation by being reintroduced to the aluminum or steel industries. The arsenic found in the baghouse dust, however, would not meet the proposed treatment standards for K088, making the regulatory status of this material unclear at best. In fact, if the baghouse dust were to be reclaimed and sent back to the aluminum industry, it is likely that the arsenic would violate the “along for the ride rule” [United States v. Marine Shale Processors, 81 F.3d at 1366, “[a] substance cannot be an ingredient in making something if it is merely along for the ride”], since it performs no function nor does it contribute in any way to aluminum or other metals manufacture. In addition, this vitrification technology must be looked upon as combustion or incineration based. As such, a host of issues must be taken into account, including permitting status, imposing MACT Waste Incinerator Standards, and cleanup of the combustion off-gases.

With this in mind, Global Environmental began an investigation of the utility of gasification for the treatment of SPL. Based on very positive initial results, Global Environmental believes the issues mentioned above would be resolved by the gasification of the Spent Aluminum Potliner thereby producing a Synthesis Gas and a vitreous frit as value added products.

THE ENTRAINED FLOW GASIFICATION PROCESS

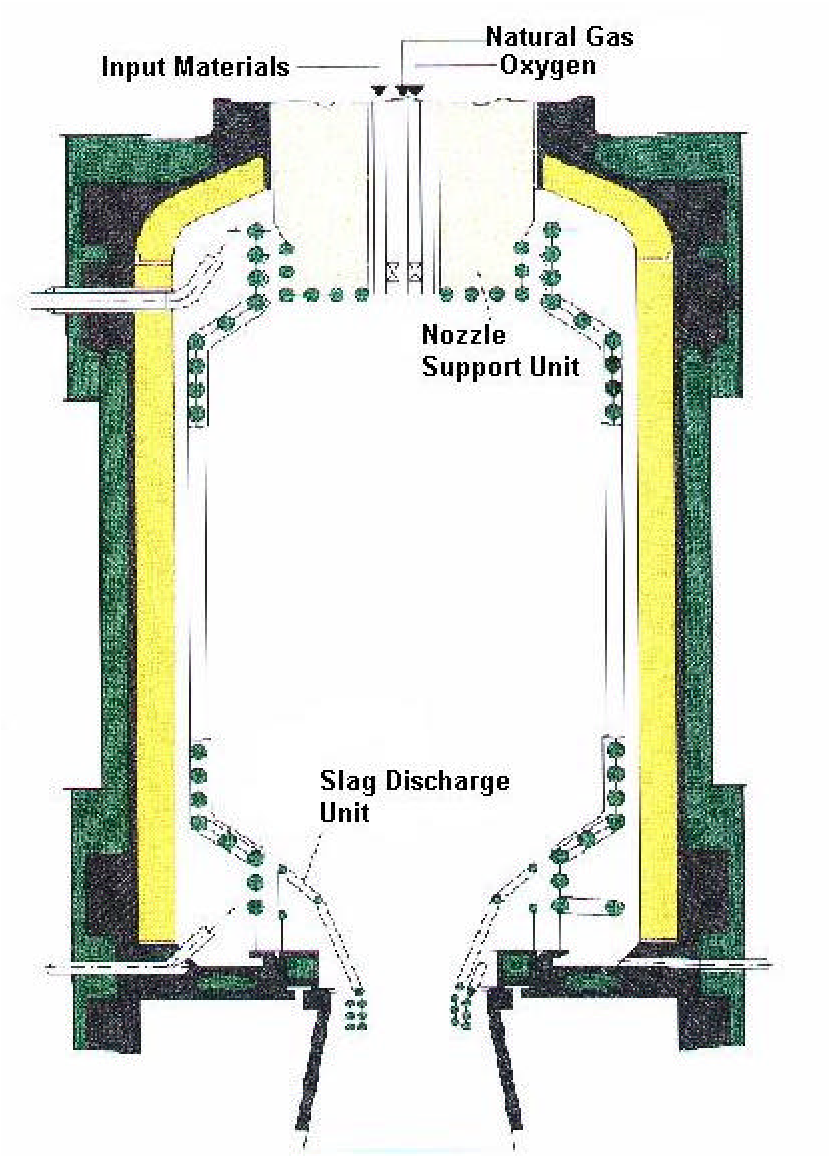
Gasification is a well-proven process for converting materials, including waste materials, to Synthesis Gas, a commodity that can be used to produce fuels, chemicals, intermediate products, or power. There are multiple, different gasification technologies that have been developed worldwide. Each of these technologies has characteristics, operating features, and specific benefits that are unique to the individual technology under consideration. Some gasification technologies developed include: entrained flow, slurry feed, multi-stage slurry feed, and fixed bed gasification systems with multiple variations being possible. These technologies fall under the general description of modern slagging gasification as specifically defined by the Gasification Technologies Council.[7]

Detailed consideration of the physical and chemical characteristics as well as the as-received form of the K088 led to the conclusion that a dry entrained flow gasification technology would be most appropriate for this technology demonstration program. There were two dry slagging gasification technologies that were considered as being the most appropriate for the gasification of K088. These two technologies are the BGL and the Noell gasification technologies. Use of the BGL technology would require that the K088 together with coal or Petroleum Coke be formed into briquettes resulting in an added investigative and processing step. For this initial program, Global Environmental decided to investigate the gasification of K088 via the entrained flow gasifier system developed by Noell – Babcock Borsig Power. Extensive technical discussions with Dr. Manfred Schingnitz of Noell indicated that their entrained flow gasifier with cooling screen was a good candidate for this test program, and the initial tests were conducted at the Noell facility in Freiburg, Germany.

The cooling screen gasifier (shown below in Figure II) is preferred if the input materials to be gasified contain greater than 1 – 1.5 percent of ash solids. Since the K088 contains substantially greater than this level of ash solids, the cooling screen configuration was selected. It is assumed the reader is familiar with the operation of an entrained flow gasifier of this type.

Briefly, the gasification chamber is constructed of steel and designed to be operated at elevated pressures (in this case approximately 380 psi) and temperatures. In this case, the volume of the gasification chamber is approximately 270 liters. The materials to be gasified are co-injected (along with oxygen, steam and natural gas – used to stabilize the reaction zone) via a nozzle located at the top of the unit. Upon entry into the reaction chamber, the materials instantaneously react at temperatures of approximately 1400 – 1600^0 C, forming a Synthesis Gas composed primarily of carbon monoxide and hydrogen and a molten slag composed of the inorganic (ash) components of the feed materials. The wall of the reaction chamber is composed of a cooling screen of pressurized, water-wall tubing, which is studded and coated with a high temperature castable refractory compound. A layer of molten slag will solidify on the refractory, thereby forming a protective coating. Additional molten material flows down this solidified slag and ultimately is quenched at the quench zone of the gasifier along with the generated, raw Synthesis Gas. The quench zone is located below the reaction chamber. The raw Synthesis Gas exiting the reaction chamber is sprayed and saturated in the quench zone with a cooling water spray before exiting the gasifier. The slag exiting the reaction chamber falls into the quench bath at the bottom of the quench zone, where it solidifies and fractures, forming a glassy, vitreous frit. The quenched Synthesis Gas exits the gasifier, where it is processed in a series of downstream gas cleanup trains. Once thus cleaned, the Synthesis Gas in the test facility ultimately exits the facility through a flare system designed to meet rigorous German environmental protection standards. The frit periodically is discharged from the gasifier through a series of lock valves prior to discharge into a slag handling system.

Figure II
Entrained-Flow Gasification Reactor with Cooling Screen



K088 SIZING AND FEED SYSTEM

Prior to gasification, the K088 was sized appropriately in order to be fluidized for the entrained flow injection nozzle. With considerable background in the gasification of a variety of organic materials including highly reactive brown coals, sewage sludge solids, and less reactive hard coals, it was believed that the carbon component of the K088 would exhibit relatively low reactivity. Hence, would need to be sized to very small diameter particles. The K088 received from the manufacturer exhibited a very large size distribution from < 20 mm (55 % of the K088) to large blocks (45 % of the K088). The entire lot of the received K088 (excluding contained chunks of aluminum) was sized in order to achieve as homogeneous and representative a lot as possible. Such sizing was accomplished by use of jaw crushers, flat-cone crushers, and/or ball mills as appropriate. The obtained particle size distribution is shown in Table III.

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Table III
K088 Particle Size Distribution After Milling

Particle Size Class (in mm) from	to	Weight Fraction Wt. %	Distribution Function %
	0.036	63.01	63.01
0.036	0.054	15.89	78.90
0.054	0.071	5.21	84.11
0.071	0.09	8.67	92.78
0.09	0.16	6.11	98.89
0.16	0.25	1.11	100.00
0.25		0.0	100.00

****

Pilot plant fluidization tests were carried out utilizing nitrogen as the carrier gas. Fluidization was achieved with a fluidizing gas velocity of approximately 1.8 cm/sec and a flow density of 449 kg/m^3. For the actual gasification test, a K088 feed rate of approximately 527 kg/hr was used.

For purposes of this demonstration program, gasification was initiated utilizing natural gas flow through the nozzle only. When stable operation on natural gas was achieved, fluidized flow of the K088 in nitrogen carrier gas was commenced. After a period of balancing and adjusting feed rate parameters, a period of stable operation was obtained, during which time samples were taken to determine operating parameters for the gasification of K088.

RESULTS

SYNTHESIS GAS

The test program shows conclusively that K088 may be gasified and converted to a Synthesis Gas, in spite of the fact that the carbon contained within the SPL exhibits exceedingly low reactivity as expected. Approximately 54 percent of the SPL contained carbon was converted to Synthesis Gas components, while approximately 44 percent was carried over to, and deposited within, the process water solids and approximately 2 percent was found in the vitreous frit. The Synthesis Gas composition may be found in Table IV below.

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Table IV
Raw Synthesis Gas Analysis

Component	**Volume Percent**
Hydrogen	17.1
Carbon Monoxide	32.5
Carbon Dioxide	19.4
Nitrogen	30.9
Hydrogen Sulfide	<150 mg/m^3
Carbonyl Sulfide	<268 mg/m^3
Fluoride compounds	< 1.0 mg/m^3
Hydrogen Cyanide	< 0.4 mg/m^3
Calorific Value	215 BTU/scf

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The elevated level of carbon dioxide in the Synthesis Gas is due in large part to the observed low reactivity of the SPL carbon, resulting in a portion of the SPL carbon not participating in the gasification reactions. It should also be noted that the gasification unit was somewhat oversized for the input material flows, the cooling screen has significant associated heat loss, and the solids or ash content of the feed is significant, which combine to give relatively larger heat loses during the course of the reaction. This must be compensated for by a higher conversion to carbon dioxide, increasing the heat release from the conversion reactions, at the expense of the desired Synthesis Gas composition. It is believed that these factors will be overcome by suitable modifications of gasifier geometry and material flows in a commercial scale gasifier. The hydrogen sulfide and carbonyl sulfide concentrations listed in Table IV were determined in the raw Synthesis Gas and were basically non-detectable within the product Synthesis Gas. Neither sulfur component could be identified in the final Synthesis Gas product. It is significant that no detectable fluorine components were identified in the Synthesis Gas, including fluoride salts, hydrogen fluoride, or any fluorocarbon compounds such as any Freon. Because of the extensive cleanup trains present, it was expected that no fluoride salts or hydrogen fluoride would be detected in the clean Synthesis Gas. Likewise, the production of compounds with a carbon-fluorine bond was not expected. No other organic compounds (such as PAHs, PCBs, dioxins or furans) were detected in the product Synthesis Gas, consistent with the gasification reports of other investigators that such materials are not formed nor detected. The metals content of the product Synthesis Gas was at or below the level of detection for the individual metals. Most notably sodium, which is present in the input K088 at a high concentration, was not detected in the product Synthesis Gas. Particulate matter within the Synthesis Gas, as expected, was low (0.2 mg/m^3) as a result of the various scrubbing and cleanup trains.

VITREOUS FRIT

The solid products containing the mineral or inorganic portion of the K088 accumulated in two forms during the gasification process – one as a granular, vitreous frit and the other as the much finer sized process- (or waste-) water solids. Aside from the Synthesis Gas, the other value added product obtained from the gasification of K088 is the vitreous frit. This frit accumulated in the form of black sand-like particles in the frit discharge system. These particles had the appearance of being melted and fused indicating that the desired slagging gasification did take place in the unit. The particle size distribution of the frit as listed in Table V is consistent with participation in slagging gasification reactions.

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Table V
Vitreous Frit Particle Size Distribution

Particle Size Class (in mm) from	to	Weight Fraction Wt. %	Distribution Function %
	<0.056	1.03	1.03
0.056	0.09	2.00	3.03
0.09	0.16	10.23	13.26
0.16	0.26	25.29	38.55
0.25	0.50	36.67	75.22
0.50	0.63	2.12	77.34
0.63	1.00	8.31	85.65
1.00		14.35	100.00

****

Note that the particles are skewed to significantly larger sizes for the frit than for the input K088, confirming that slagging gasification had taken place. This causes the particles to immediately settle out in the frit collection system rather than being entrained with the wastewater flow (as is the case with the wastewater solids – see discussion below).

The composition of this vitreous frit is presented in Table VI. Note that the ash analysis of this frit is similar, but not identical, to the ash analysis of the input K088. The vitreous frit accumulated at the rate of approximately 194 kg/hr, consistent with the 54 percent carbon gasification conversion noted above in the discussion of the Synthesis Gas. Note, however, that some vitreous frit was retained within the frit handling system and not accounted for here.

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Table VI
Analysis of Vitreous Frit from the
Gasification of Spent Aluminum Potliner
(in weight percent unless otherwise noted)

Proximate Analysis:	
Moisture	6.1
Ash	91.9
Volatiles	0.4
Fixed Carbon	1.6
Ultimate Analysis:	
Carbon	1.6
Hydrogen	0.2
Oxygen	0.0
Nitrogen	0.0
Sulfur	0.2
Fluorine	14.1
Cyanides (mg/kg)	20.3
Arsenic (mg/kg)	11.0

Ash Analysis:	
SiO_2	19.0
Al_2O_3	35.7
Fe_2O_3	4.5
CaO	4.6
MgO	0.6
SO_3	0.2
TiO_2	0.4
P_2O_5	0.7
Cr_2O_3	<0.1
MnO	<0.1
V_2O_5	<0.1
Na_2O	20.8
K_2O	0.5
Melting Point: deg C.	1430

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VITREOUS FRIT LEACHING CHARACTERISTICS

The leaching characteristics of the vitreous frit are of significant interest, particularly considering the reported[13] leaching characteristics of the residue from the Reynolds' Gum Springs SPL process. EPA has indicated that the leaching profile of K088 vitreous frit into neutral distilled water would be more indicative of the real life characteristics of the vitreous frit than leaching into the acid buffered solution called for in the TCLP procedure. The results of this modified TCLP leaching profile (into distilled water) are presented in Table VII.

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Table VII
Leaching Characteristics of K088 Vitreous Frit
TCLP Method – Modified with Distilled Water

Final pH 7.97

Component	**Concentration (in mg/L)**
Cyanide (total)	0.014
Cyanide (amenable)	<0.005
Fluoride	180.0
Antimony	0.0098
Arsenic	<0.005
Barium	<0.010
Beryllium	0.0085
Lead	<0.005
Cadmium	<0.001
Chromium	<0.005
Nickel	<0.005
Mercury	<0.0002
Selenium	<0.001
Silver	0.013
Thallium	<0.001
Vanadium	<0.030
Zinc	<0.02

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Note the low level of leaching of cyanide (0.014 mg/L), arsenic (<0.005 mg/L), other metals, and even fluoride (180 mg/L) into the distilled water. The 180 mg/L concentration of fluoride in the leachate is remarkable given the fact that the fluoride content of the vitreous frit is exceptionally high at 14.1 percent (141,000 parts per million). When compared against the treatment standards for Spent Aluminum Potliner and the results reported from the monofill receiving the residue from the Reynolds process, these results are very encouraging, indicating that the slagging gasification of Spent Potliner accomplished, to a great extent, the hoped for encapsulation of the constituents of concern within a glassy matrix, rendering them essentially non-leachable.

Given the fact that the Reynolds Gum Springs process residue was found to leach more fluoride at the elevated pH found at the monofill facility[13], it was important to identify the effect differing pH levels might have on the leaching of fluoride from the vitreous frit. Data show that the ability of fluoride to leach from the vitreous frit was directly related to the final pH of the solution. This is shown in Figure III below. At elevated pH levels (i.e., pH 9.75 in the basic range), the ability of fluoride to leach from the vitreous frit is substantially greater than at lower pH levels near a pH of 7. Even though there is a definite correlation with pH, it appears that the ability of the vitreous frit to leach fluoride is substantially lower than has been reported[13] for the Reynolds residue. In fact, it is remarkable that the leaching of fluoride from the vitreous frit is so low given the high, 14.1 % fluoride content of the frit. Additional investigation would be required to determine the empirical relationship between leaching and pH. We are optimistic that suitable modifications to the gasifier design and/or operating parameters will significantly decrease the ability of fluoride to leach from the vitreous frit, further improving the utility of gasification for the beneficial recycling of Spent Aluminum Potliner material.

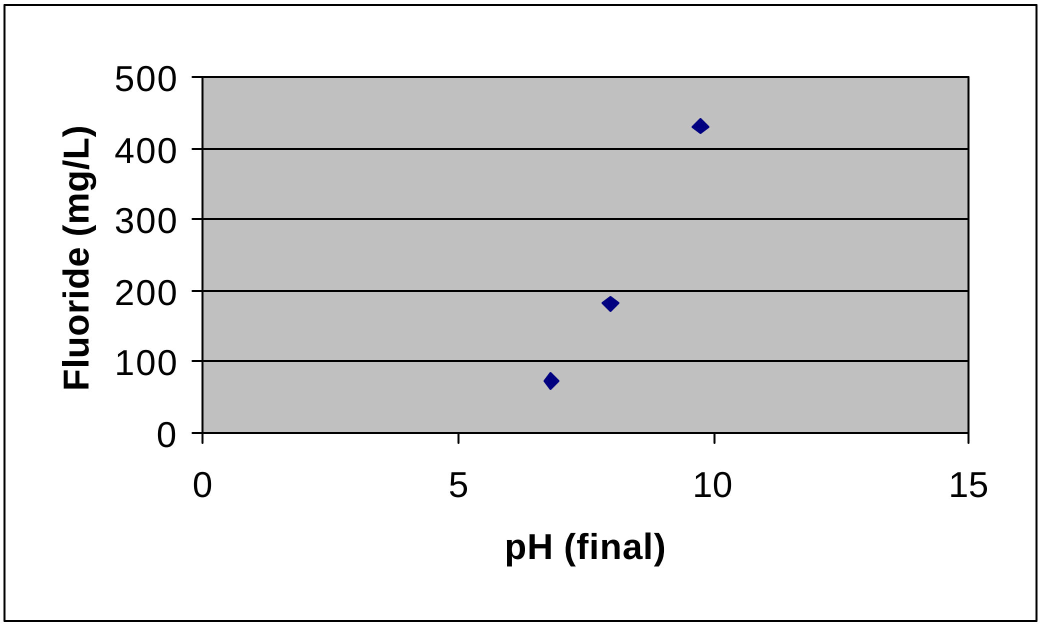

Figure III

PROCESS WATER SOLIDS

Process water solids represent the remaining fraction of the solid product materials containing the inorganic components of the Spent Aluminum Potliner. Unlike the vitreous frit, this material did not appear to have participated in the slagging gasification reactions at all. The material was essentially unchanged in appearance from the input K088 and was of similar composition (see Table VIII below), specifically in terms of carbon content. The process water solids were generated at a rate of approximately 218.7 kg/hr, slightly more than the production of vitreous frit. Although the process water solids may be recycled back to the gasifier to provide for complete recycle of the SPL, an investigation is planned to modify the gasifier geometry and/or the gasification parameters in order to achieve 100 percent gasification of the SPL in one pass.

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Table VIII
Analysis of Process Water Solids From Gasification of Spent Aluminum Potliner

(In weight percent unless otherwise noted)

Proximate Analysis:		**Ash Analysis:**	
Moisture	NA	SiO_2	13.9
Ash	65.36	Al_2O_3	35.6
Volatiles	6.16	Fe_2O_3	3.2
Solids	NA	CaO	2.5
Fixed Carbon	NA	MgO	0.4
		SO_3	1.2
Ultimate Analysis:		TiO_2	0.3
Carbon	28.48	P_2O_5	<0.1
Hydrogen	0.4	Cr_2O_3	<0.1
Oxygen	NA	MnO	<0.1
Nitrogen	NA	V_2O_5	<0.1
Sulfur	1.2	Na_2O	19.0
Fluorine	15.7	K_2O	0.4
Cyanides (mg/kg)	12.2		
Arsenic (mg/kg)	14.0		

NA = Not Available

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For completeness, it should be noted that the process water, itself, contained no significant quantity of cyanides, sulfide, metals, or other constituents of concern. The fluoride concentration in the process water was only 160 mg/L (at about the level determined for the fluoride leaching from the vitreous frit into distilled water) and the sodium concentration was at 3,180 mg/L; elevated but not of great concern.

CONCLUSIONS

As gasification has become more widely accepted, investigators keep expanding the list of materials that have been gasified successfully. As an industry, gasification has moved beyond the feedstock limits of coal, Petroleum Coke,Bio-Mass Solids, and Municipal Solids Wastes. Increasingly, industrial chemical waste streams have been demonstrated to be excellent candidates for gasification. Materials such as secondary refinery materials, nitrogen-bearing organic liquids, and highly chlorinated liquid wastes have been gasified, with no adverse environmental consequences encountered.

The results of this initial study show conclusively that Spent Aluminum Potliner (K088), a solid waste generated during the manufacture of aluminum metal, may be beneficially recycled by gasification. The product Synthesis Gas may be utilized for any of a myriad of uses typical for Synthesis Gas. The vitreous frit product has been shown to pass current and expected EPA-mandated treatment standards for K088. Neither cyanide nor arsenic were detected at any significant levels in the leachate of the TCLP test protocol or in any modified TCLP test at low neutral, and high pH levels. Even with an exceptionally elevated fluoride level greater than 14 percent, the vitreous frit showed remarkably little propensity to leach fluoride at the differing pH levels studied. In fact, the frit showed a lower leachability than residues obtained from alternate K088 treatment processes.

The carbon present in K088 (at a level of 25 percent or higher) was found to have the expected low degree of reactivity when compared to other solid feeds such as coals and Petroleum Cokes. This low reactivity resulted in about a 55 percent conversion of the K088 in the gasification reactions. Additional development activities, including reactor modifications and operating parameters are expected to significantly improve this conversion rate. In addition, such studies will be designed to improve the already excellent leaching characteristics of the product vitreous frit. Testing will be conducted with the goal of obtaining fluoride in a form that could be recycled directly to the aluminum industry, resulting in another value added product from gasification.

The results from these preliminary tests on the gasification of this rather exotic, high-fluoride, solid waste from the aluminum manufacturing industry are very promising. Together with the work of other researchers, these results show that gasification is an exciting and productive technology for the beneficial recycling of a significant number of carbon bearing waste streams. We applaud EPA's continued interest in gasification technology as a method of handling this nation's waste streams. EPA and other regulatory agencies must continue to examine this technology and its very real and substantial environmental benefits. A regulatory approach that encourages gasification, while promoting beneficial recycling and a decreased reliance on older, less environmentally sound technologies such as incineration and landfill is warranted.

ACKNOWLEDGEMENTS

The authors would like to express their sincere gratitude to the staff of Noell- Babcock Borsig Power in Freiburg, Germany for their dedication and efforts on behalf of this research program. We especially would like to thank Dr. Manfred Schingnitz, Mr. Markus Kautzsch, Mr. Lutz Hoffmann, Ms. Christine Hummel, and Mr. Ara Aghajanian for their tireless work, open exchange of ideas, enthusiasm for the project, and for their warm and kind hospitality. It has been our privilege to work with them.

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