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THERMOSELECT: ENERGY AND RAW MATERIAL RECOVERY THROUGH THERMAL CHEMICAL TRANSFORMATION IN A CLOSED-LOOP SYSTEM

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OVERVIEW

Refuse has been burned for over 100 years. About 30 years ago, the ecological burdens imposed by refuse incineration became recognized, and attempts were initiated to reduce pollutant emissions and its environmental impact by the continuous retro-fitting of new system components. The elementary incineration furnaces were soon supplemented by: downstream electrostatic filters for dust collection, wet washing devices or dry adsorbing materials to remove chlorine, fluorine, sulfur and heavy metal compounds, and post-combustion chambers to destroy organic compounds. In the last ten years, measures have focused on the fitting of DENOX systems to reduce NO_x levels and recently, the deployment of activated charcoal systems in an attempt to ensure compliance with increasingly stringent emission regulations.

The industry is also experiencing increased interest in waste to energy processes. The utilization of waste heat to gain energy by using open-combustion processes can lead to the formation of new pollutants in the hot gas stream such as dioxins and furans.

Increasingly, more stringent emissions regulations will require the continued addition of more efficient equipment. This will be the only route open to allow open-combustion systems to meet these increasingly more stringent regulations.

The end result will be the need to increase capital investment for the open-combustion process that will directly effect the operational cost per ton.

From the analysis of this situation, a new process concept was created and identified as THERMOSELECT. The concept and its implementation has been tested and developed to technical maturity in a large scale demonstration plant located in Fondotoce, Italy [1]–[5]. Its ecological advantages and process engineering reliability are clearly substantiated and certified [6]–[8].

THERMOSELECT — CONCEPT OF THE PROCESS

This paper will introduce the new approach for the treatment of solid waste. This approach has been demonstrated at the processing rate of 100 tons per day for the recovery of energy and raw materials from commingled refuse. The process utilizes a *closed-loop process design.* This process design generates only a very small volume of process gas that must be cleaned and minimizes the formation of dust, nitrogen oxides and other pollutant materials when compared to the process developed gases of open-combustion incineration.

A complete conversion of materials is achieved by the design of a continuous flow of material and energy using a *closed-loop process* combined with high temperature exposure and a long residence period. This combination destructs the most complex of organic compounds and generates a recoverable synthesis gas of value. The remaining acid gasses and volatile heavy metals are treated and recovered in-plant. Heavy metal components are recovered as a manageable and contained precipitate. The acid gases are treated and recovered as salts. Emissions are reduced dramatically and result primarily from the combustion of the clean synthesis gas which is used to produce heat and through the use of gas engines to produce electricity. The process develops adequate energy gas to operate the facil-

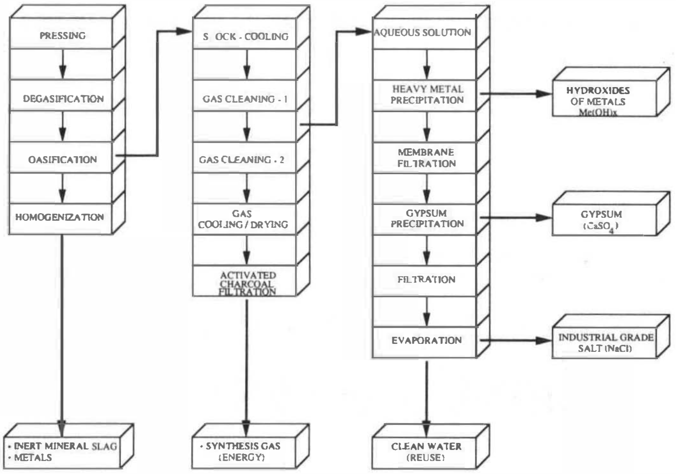


FIG. 1 THERMOSELECT PROCESS — SEQUENCE STEPS

ity (heat/electricity) and has a positive balance of electricity. Heterogeneous wastes and non gasifiable components of the waste stream can be brought over into a mineral or metallic melt and recovered as inert and non-toxic products. All process generated water is recovered, cleaned, and reused; thus eliminating the need to sewer process generated water.

The essential steps and principles of this process are: (Figures 1 and 2)

A. Commingled waste possesses a low density and requires a great deal of space. The process uses standard in-line scrap metal presses to compress the waste thus increasing its overall density. To accomplish this, presses which have been thoroughly tried and tested for over 30 years of industrial operation are used. The refuse is compacted to around 10% of its original volume. This compacting results in highly compressed packages of commingled waste where the moisture that is naturally contained in the refuse becomes evenly distributed. As a result the residual air content in the compressed refuse packages is reduced to a minimum.

B. The highly compressed refuse "packages" are then forwarded in-line directly to a pressure-resistant channel to form a gas-tight "plug." In this externally heated channel (600°C/1100°F), the refuse is intensively heated by conduction which vaporizes the volatile portion of the waste that is primarily water. The hot gas molecules, especially that of water vapor, transfer energy to further heat the waste packages. These heated gases flow through the heated channel and enter the next stage, the high temperature chamber (HTC). The organic part of the compressed packages is degassed and converted into carbon; the inorganic mineral and metal matter are entrapped with this carbonized portion.

C. As the temperature in the degassing channel reaches 600°C (1100°F); the hot carbon briquettes, with the entrapped inorganic components, are continuously moved forward to the next stage by feeding new refuse packages into the degassing channel. The gaseous components; H_2O, CO, CO_2, H_2, C_xH_y, are moved continuously from the degassing channel into the high temperature chamber (HTC).

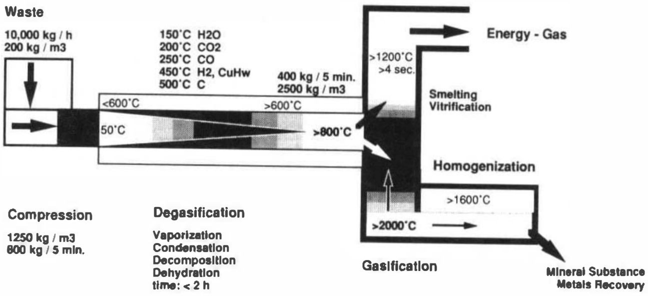


FIG. 2 THERMOSELECT PROCESS — ENERGY AND RAW MATERIAL RECOVERY

The carbon briquettes break-apart as the carbon and inorganic portions enter the high-temperature gasification chamber (HTC). Oxygen is introduced through a burner device and provides a high temperature oxygen gasification medium. Oxygen, in the presence of steam, ensures that all occurring chemical reactions take place at high speed. The essential processes follow:

- *All organic compounds are completely destroyed* and are decomposed to atomic levels (cracking).
- *A synthesis gas forms, the mechanisms are:*

  Oxidation: (exotherm reaction)

  $$C + O_2 - CO_2$$

  $$C_xH_y + (X + \tfrac{1}{4}Y)O_2 - XCO_2 + \tfrac{1}{2}\ Y\ H_2O$$

  Boudouard Reaction: (endothermal reaction)

  $$C\ +\ CO_2 - 2CO$$

  Hydrogen Reaction: (endothermal reaction)

  $$C\ +\ H_2O\ -\ CO\ +\ H2$$

  $$C_xH_y\ +\ XH_2O\ -\ XCO\ +(X + \tfrac{1}{2}\ Y)\ H_2$$

- *The Synthesis Gas Composition:* (Table I : synthesis gas analysis)

The processes for forming synthesis gas have been utilized technically for more than 60 years. Significant experience is therefore available regarding the design and safe operation of gasifiers at various temperatures and pressures.

TABLE I SYNTHESIS GAS PURITY: BEFORE/AFTER ENGINE COMBUSTION

ANALYSIS OF SYNTHESIS GAS:

		Vol %
CARBON MONOXIDE	(CO)	32 - 47
HYDROGEN	(H_2)	29 - 37
CARBON DIOXIDE	(CO_2)	19 - 29

SYNTHESIS GAS PURITY: BEFORE/AFTER ENGINE COMBUSTION

Component	Before Gas Motor mg/Nm^3	Gas Motor Exhaust 5 vol % O_2 mg/Nm^3
HCl	0.3	0.9
HF	<0.06	<0.1
HCN	<0.01	
SO_2	<1.35	<2.0
H_2S	<0.1	
NO + NO_2	<6	72.0
CO		51.0
Formaldehyde		0.08
TE PCDD/PCDF	2.0×10^{-9}	1.2×10^{-9}
Dust	<0.25	<1.4
Cd	<0.001	<0.005
Hg	<0.006	<0.009
Pb	<0.005	<0.032
As	<0.0004	<0.001
Zn	<0.0029	<0.0040
Cu	<0.0026	<0.011

TABLE II VITREOUS MINERAL PRODUCT: ANALYSIS

Analysis	Result	Unit	EPA Regulatory limit
Ignition	>200	°F	<140
Corrosivity	6.9	Ph	<2, >12.5
As Cyanide	<0.10	mg/kg	variable
As Sulfide	<0.50	mg/kg	variable
Arsenic, TCLP	<0.40	mg/l	5.0
Barium, TCLP	0.07	mg/l	100.0
Cadmium, TCLP	<0.01	mg/l	1.0
Chromium, TCLP	0.04	mg/l	5.0
Copper, TCLP	0.11	mg/l	100.0
Lead, TCLP	<0.10	mg/l	5.0
Mercury, TCLP	<0.0025	mg/l	0.2
Selenium, TCLP	<1.0	mg/l	1.0
Silver, TCLP	0.03	mg/l	5.0
Zinc, TCLP	0.22	mg/l	500.0

Source: Canton Analytical

TABLE III VITREOUS MINERAL PRODUCT: ELUTION TESTING

Parameter	Mass %
Hi-ignition loss	100.8
Si(SiO_2)	44.7 - 51.5
Al(Al_2O_3)	14.2 - 16.0
Ca (CaO)	12.7 - 14.6
Na (Na_2O)	4.5 - 5.5
Fe (Fe_2O_3)	4.8 - 14.0
K (K_2O)	1.4 - 1.5
Mg (MgO)	2.6 - 3.0
P (P_2O_5)	0.5 - 0.9
S(SO_3)	0.09 - 0.13

Parameter	Mass %
C	0.05 - 0.12
Hg	$<5. \times 10^{-6}$
Sn,Tl, As	<0.01
Sb,Pb,Ni	<0.01
B	0.03 - 0.04
Zn	0.010 - 0.055
Cr	0.07 - 0.36
Ba	0.18 - 0.32
Mn	0.20 - 0.23
Cu	0.04 - 0.10

- Non-gasifiable ingredients are liquefied and are refined by oxidation thus all entrapped carbon is totally reacted. This results in a molten mass of metal equal to that of the input waste and in mineral substances also corresponding to the mineral content of the waste input. The necessary melting energy is supplied by the exothermal reactions. The metal/mineral product is recovered in the form of an inert and non-toxic vitreous material that meets TCLP elution test standards (Tables II and III). The metallurgy and glass industries have developed methods for converting these materials into usable products. THERMOSELECT continues its development to produce marketable products from these materials.
- Inorganic components that are carried along with the synthesis gas into the upper section of the high temperature chamber are vaporized due to the high temperatures (1200°C/2192°F). These materials are captured and secured in the gas cleaning section of the process.

D. Degasification with the exclusion of air followed by a continuous flow of carbon and gasification with high temperature oxygen results in a raw synthesis gas volume of about 1000 Nm^3 per Mg (1 metric ton) of waste input. The main components of the synthesis gas are carbon monoxide and hydrogen (Table I) . The synthesis gas and other components of the gas stream at a temperature of 1200°C (2192°F) exit the HTC and are shock-cooled to below 90°C (194°F) using a water flush.

Liquid melt mineral particles and in some circumstances traces of carbon that can be carried along with the gas, are precipitated in water and are separated and recycled back into the thermal process. The rapid cooling of the hot gas stream in the absence of oxygen prevents a "de-novo" synthesis (formation of chlorinated hydrocarbons) that can form dioxin and furan compounds from taking place. In the first gas wash traces of accompanying metals or metal compounds are precipitated and flow with the aqueous fractions of hydrogen chloride and hydrogen fluoride to the next multi-stage alkaline gas wash. The multi-stage alkaline wash assures the separation of sulfur compounds. The synthesis gas is separated prior to this second gas washing stage and separately cleaned and cooled to reduce its residual moisture. The final purification of the synthesis gas is concluded by passing the gas through an activated charcoal filter. The use of activated charcoal filters for the final purification of oxygen-free synthesis gases at temperatures far below 80°C/176°F is a process and safety advantage. The low volume of gas produced, when compared to conventional technologies for flue-gas purification, allow the entire system of gas purification using this process to be smaller by a factor of ten (10).

E. The aqueous acid washing solutions generated during the gas cleaning process are subjected to conventional chemical material separation processes. After the heavy metal compounds have been separated, calcium ions are added to separate the insoluble compounds. When the residual solutions are concentrated by evaporation, a sodium salt concentrate is obtained. Products from the gas cleaning and water recovery process include; industrial grade sodium chloride (salt), industrial grade calcium sulfate (gypsum) or elemental sulfur and a separate precipitate containing the heavy metals from the input waste. This heavy metal precipitate requires special handling under today's regulations. All of the remaining water from this process is recovered and reused within the system, no process water is sent to the local sewage system.

F. In a standard facility, the synthesis gas is transformed directly into electrical energy using generators that are driven by gas motors. The synthesis gas also contributes to the heating of the degassing channel. Since the synthesis gas contains a large content of carbon monoxide (CO) and hydrogen (H_2) it can also be used to produce alternative fuels such as methanol and/or benzene. However it should be noted that a considerable expenditure of energy is necessary to synthesize methanol.

MASS AND ENERGY FLOWS

The mass and energy flows are shown in Figures 3 and 4. They assume that an average composition of the waste contains 600 kg organic substances, 200 kg inorganic substances and 200 kg of water. It is clear that decisive advantages exist compared to conventional thermal processes:

- The process is a closed material conversion system for recovering energy and raw materials from wastes. The process is flexible enough to operate with or without pre-separation of the waste stream thus offering another option for the recovery of energy, the recovery and recycle of materials contained in solid waste without the intensive labor, energy consumption and the noise and odors common to most material recovery facilities (MRF).
- The thermodynamics-kinetic conditions that include temperatures >1,200°C/2192°F combined with a gas retention time in excess of 4 seconds at these temperatures guarantee the complete conversion of all organic components into a synthesis gas. Since oxygen is used as the gasification medium, the total volume of gases generated is small when compared with flue gases. Consequently, after purification the synthesis gas can be used as a raw material for the direct recovery of energy without intermediate storage.
- The in-line, continuous flow operation of this process exposes all the waste to the high temperatures. The non-gasifiable waste components are liquefied. The elements silicon, aluminum and iron, together with the oxides of manganese, and others, form a stable vitrified mineral system which can be used without restriction as an ecologically safe end-product.

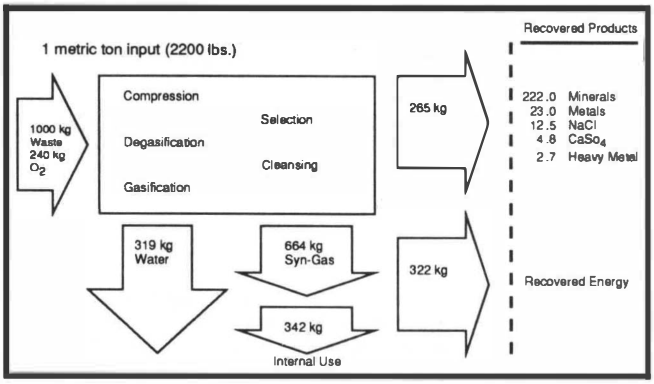


FIG. 3 MASS FLOW

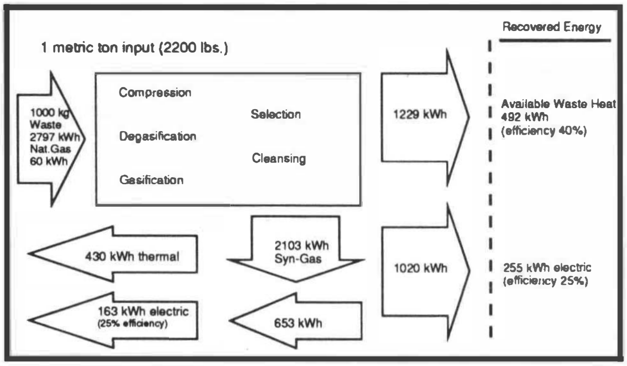


FIG. 4 ENERGY FLOW

- Typical alloy forming elements, nickel, chromium, copper and the like become components of an iron alloy containing greater than 90 weight percent of iron.
- The molten mineral substances and the molten iron alloy separate from one another due to differences in melt viscosity, density and surface tension. Separation is easily accomplished by the introduction of the combined hot melt into a water vessel; this results in the metal forming round pellets of steel alloy and the mineral component forming a fine granulated glass-like product. Final separation of the metal is accomplished using magnetic separation.
- The purification of the synthesis gas using a wet-wash process makes it possible to transfer the contamination in the gas stream into the aqueous phase; this allows for their joint chemical separation into metal hydroxides, a mixture of calcium sulfate fluorides and a sodium chloride concentrate. Using this procedure, the concentrated heavy metals are ready for further hydro-metallurgical or thermal processing to produce usable metals or metal compounds, the sodium chloride component is ready as diluted raw salt for chloro-alkali electrolysis. The total quantity of residues from the purifica-

tion of the process water corresponds to the quantities which are usually derived from the purification process for standard flue gas systems.

- The utilization of the synthesis gas to heat the degassing channel and the complete conversion of the balance into electricity provides the heat and electricity requirements for the entire plant with a positive balance remaining. If a facility with a capacity of 150,000 Mg per year (165,000 short t/y), is operated at full capacity using the waste mixture identified earlier, there is ~6 MW positive of electrical power available for outside plant use.
- The following coefficients are an example used to facilitate comparative considerations with other technologies for utilizing waste:

  - Energy coefficient, E_k = surplus energy/quantity of ecologically safe materials
  - Ecological coefficient, O_{ek} = surplus energy quantity of emitted pollutants
  - Investment coefficient, I_k = surplus energy/investment expenditure × time

Such a mode of consideration permits rapid comparison between various technologies. If all of the expenditures for pre-treatment and post-treatment of waste are included in the energy balance, one finds objective information about the advantages and disadvantages of existing or future concepts of solid waste treatment.

ANALYSIS OF THE PRODUCTS OF THE PROCESS

Synthesis Gas

By generating synthesis gas it becomes possible to utilize the main portion of the energy stored in residual waste. The main components of the synthesis gas are as follows:

	Volume %
CO	32–47
H_2	29–37
CO_2	19–29

Residual nitrogen and water vapor in single digit percentage quantities are contained as secondary components. The heat value of the gas approximates 10,000 kJ/Nm^3 (2,390 $kcal/Nm^3$). As a result of the extensive cleaning and purification of the gas the amount of contaminants in the gas is very small.

The low concentrations of contaminates observed in the purified synthesis gas lead one to expect emission values which lie clearly below existing limit requirements. This can be expected regardless of the chosen combustion process: gas motor, industrial firing or steam generator. The synthesis gas contains no significant concentrations of materials whose combustion could lead to reactions capable of forming significant amounts of, as an example, dioxins, furans and/or other organic compounds.

The content of nitrogen oxides in the combustion exhaust gases derived from the utilization of the synthesis gas is determined more by the chosen combustion conditions then by the contaminates contained in the synthesis gas. The main components of the synthesis gas are carbon monoxide and hydrogen and this results in a combustion exhaust gas that is low in NO_x.

Vitreous Mineral Product

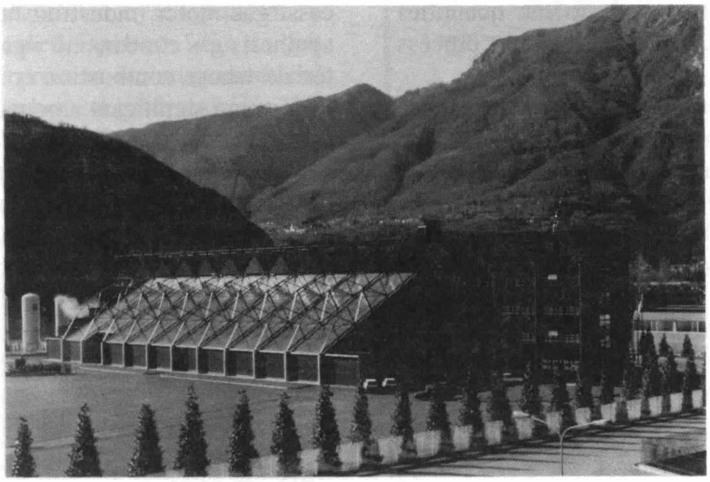
In contrast to previously customary combustion processes, the THERMOSELECT process, with a continuous flow of material and energy and optimal energy utilization, results in directly usable vitreous mineral substances. Their stability as an additive for concrete is proven. The mineral substances replace natural stone [8]. Analytical testing of the mineral composition confirm the substances to be elute-stable and environmentally stable materials.

The values shown for the annealing loss is based on a weight increase through oxidation at a temperature of about 1000°C. A low content of residual carbon is achieved and the traces of heavy metals, which are minimal, are solidly bound. These factors are of basic significance for the quality of the mineral substances. The analytical composition of the mineral substances in the granulate corresponds with that of previous studies of similar products. The basalt-like vitreous mineral product demonstrates a high degree of inertness which yields favorable elution properties. This material should meet the most difficult elution requirements allowing it to be stored and used without special protective precautions [6], [8]. Table III: Elution parameters of the Vitreous Mineral Product.

Recovered Metal Alloy

The metal resulting from this process is a low-alloy iron (>90%, weight) with the following approximate additional elements. This metal is recycled as a raw material using standard metallurgical processes.

	weight %	relevant ecological elements:	weight %
copper	~5	thallium	0.01
nickel	~0.3	cadmium	< 0.001
chromium	~0.3	lead	< 0.08
tin	~0.4	mercury	< 0.00001
phosphorous	~2.0	arsenic	< 0.05



THERMOSELECT Demonstration Plant
>100 short tons per day

Quality of the Process Water after Condensation

The process water solution after treatment to remove each of the contaminant products is reduced in volume by evaporation in order to concentrate the remaining sodium salts. The water re-enters the process water loop for reuse in the water cooling and washing stages.

DEMONSTRATION PLANT — FONDOTOCE, ITALY

The THERMOSELECT concept was developed in several pilot stages up to a capacity of 1000 kg per hour. The demonstration plant was built in Fondotoce, Italy within a period of only six months using a module design concept. It has a 4.2 Mg per hour (~100 metric ton/day) operation permit and has been in operation since 1992, under various load conditions. The resulting information, data and experience have led to reliable design criteria for a large scale commercial plant having a disposal capacity of 150,000 metric tons/year (480 metric tons /day) i.e., 2 lines × 10 metric tons/hour. The modular mode of construction allows that plants of this design and size can be built and put into operation within a construction period of one year.

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