R'02

- Recovery
- Recycling
- Re-integration

6th World Congress on Integrated Resources Management
February 12 – 15, 2002 in Geneva, Switzerland

more

THERMOSELECT - AN ADVANCED FIELD PROVEN HIGH TEMPERATURE RECYCLING PROCESS

H. K. Mucha, Dr. U. Drost
Thermoselect S.A., Via Naviglio Vecchio 4, CH-6600 Locarno

Over the past decade, an innovative waste recycling technology –the THERMOSELECT process– has been developed, proven in a large scale demonstration facility and commercialized by the THERMOSELECT S.A. company. Solid wastes, including MSW, are continuously processed in a fixed bed oxygen blown gasification and residue melting reactor to achieve a maximum recovery of recyclable raw materials, with simultaneous utilization of the chemical energy contained within the waste material and minimum impact to the environment. Commercial plants have been recently erected in Karlsruhe, Germany, and in Tokyo-Chiba, Japan. The Karlsruhe plant has a waste treatment capacity of 720 Mg/d and the Chiba plant of 300 Mg/d.

PROCESS DESCRIPTION

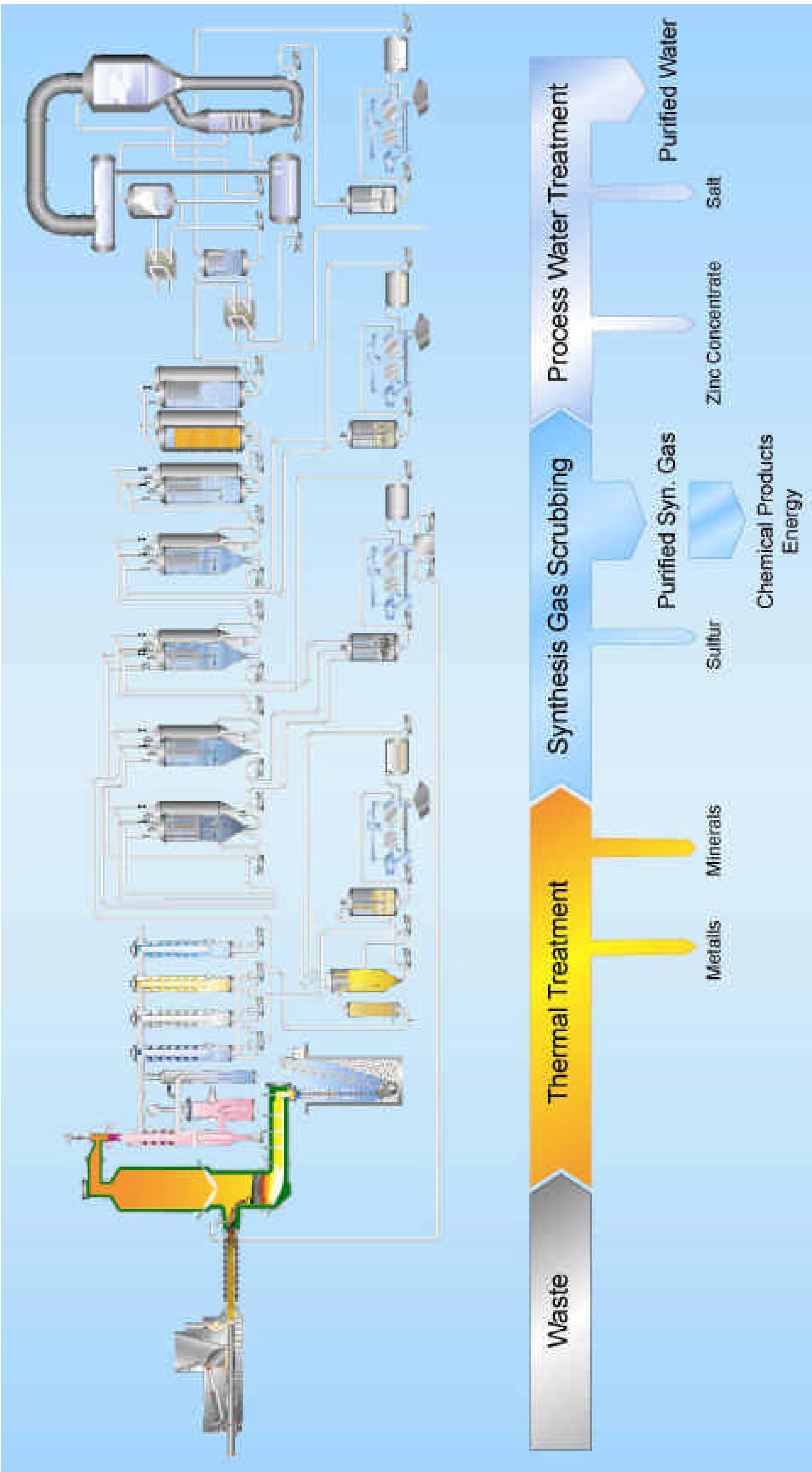
The THERMOSELECT Resource Recovery Facility recovers pure synthesis gas, useable vitreous mineral substances and iron rich materials from mixed wastes such as Muncipial Solid Waste (MSW) and Commercial and Industrial Wastes. In an uninterrupted recycling process the organic waste fractions are gasified and the inert materials are simultaneously molted down. The subsequent purification of the synthesis gas and process water yields clean water, salt, zinc concentrate and sulfur as products. In contrast to other processes, no ashes, slags, inerts, chars or filter dusts have to be deposited in a costly manner or subjected to secondary treatment.

Waste Feed System

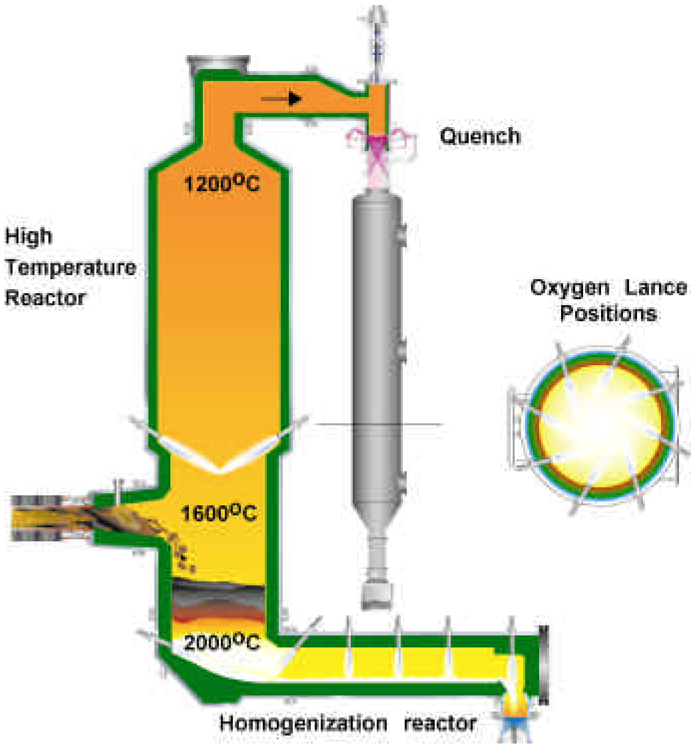
In the first process step the untreated as received municipal solid waste is discharged directly into a storage bunker. The bunker has about 5 days storage capacity and is used to dampen out fluctuations in waste receival cycles. A grapple crane is used to transfer the waste to the feed chute of the bailing press. The press in turn compacts the waste, distributes liquid within the bail and forces out the residual air (nitrogen ballast). Dense waste plugs are thus formed which are fed one after the other into the degassing channel of the reactor. These waste briquettes also form the seal of the reactor at the inlet.

Gasification of waste

The press is directly connected to the degassing channel. The channels cross sectional area increases slightly as the gasification reactor is approached, which eases the movement of the waste plugs and the transportation of the gases (evaporation of water, pyrolysis and synthesis gases) from the waste into the reactor.
Radiated heat from the gasification reactor initiates the waste drying and decomposition processes in the degassing channel and are brought to completion within the reactor itself. The dried and charred briquettes emerge from the degassing channel and are exposed to steam (from water in the waste) and controlled injection of pure oxygen as the gasification medium.



THERMOSELECT Resource Recovery Process



All organic materials in the waste are transformed into a synthesis gas with a composition that reflects the thermodynamic equilibrium of the temperature at the top of the reactor (approximately 1200°C).

The high temperature, oxygen free environment and long residence time of 2 seconds in the upper part of the reactor ensures that only small molecular species such as H_2, CO, CO_2 and H_2O leave the reactor as prime constituents of the synthesis gas. The main prevailing exothermic reactions occurring in the upper part of the reactor are:

$C + ½O_2$? CO

$C + O_2$? CO_2

$2C_xH_y + (2X+Y/2)O_2$? $2x\ CO_2 + yH_2O$

with a simultaneous endothermic Boudouard reaction, e.g.

$C + CO_2$? $2CO$

and the endothermic water shift reaction

$C + H_2O$? $H_2 + CO$

$C_xH_y + X\ H_2O$? $(x+Y/2)H_2 + XCO$

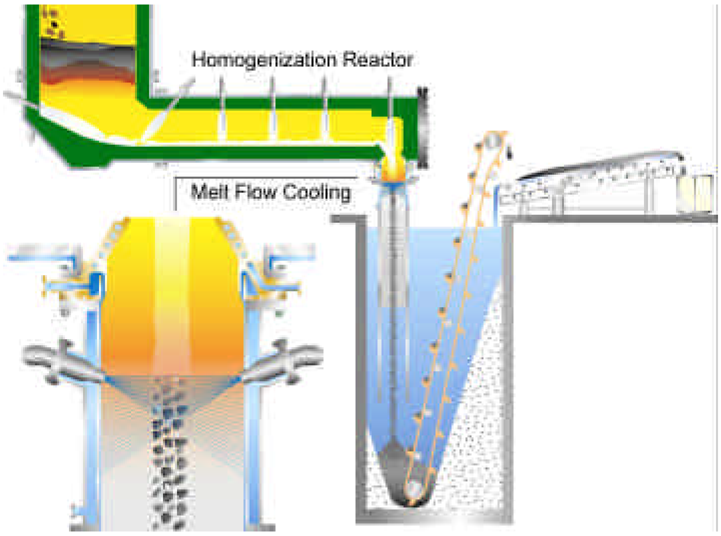
After gasification at a gas exit temperature of 1150-1200°C, a synthesis gas is obtained being typically composed of 25-42 Vol.-% H_2, 25-42 Vol-% CO, 10-25 Vol.-% CO_2 and nitrogen.

Melting of inorganic materials

In the lower part of the reactor all metallic and mineral components are molten. Metals such as mercury, zinc etc are volatilized at the high temperatures in the lower part of the reactor (locally up to 2000°C) and are extracted with the synthesis gas. The oxides of the base metals form a mineral melt in the lower part of the reactor. Simultaneously other metals are also molten down. A typical iron alloy is formed containing nickel, copper and traces of other heavy metals. The typical iron content is more than 80%.

The mineral and metal melts collect in the lower homogenization reactor, which is heated with natural gas and oxygen. A two phase flow occurs in the melt with the minerals and metals separating automatically as a result of the differences in relative density (RD 3 and 7 respectively). Any residual carbon in the melt is synthesized to further syngas.

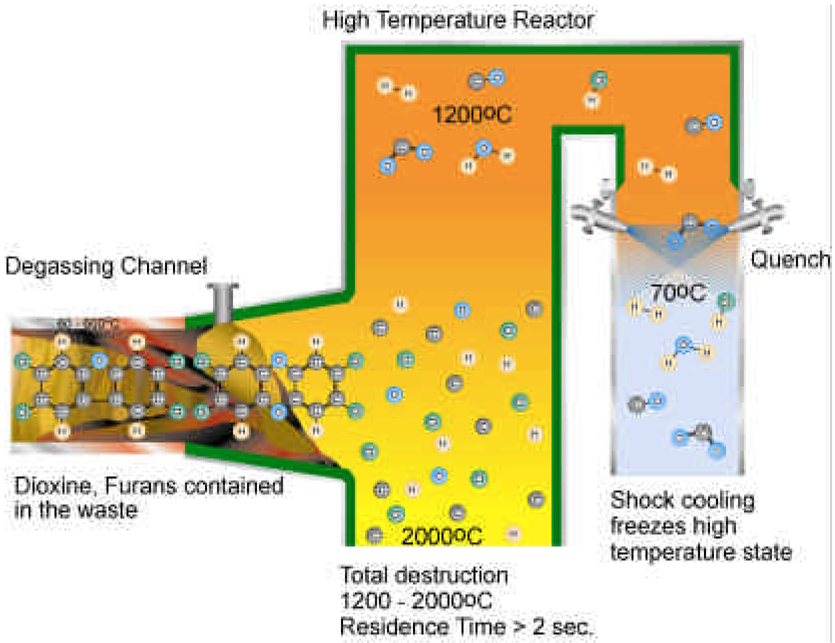
The molten substances are then granulated by water quenching and extracted from the quench basin using a bucket elevator. The difference in thermal conductivity between mineral and metal melt results in the two products automatically granulating separately within the same quench basin. The metal granules are then separated from the mineral granules by magnetic separators.



Synthesis gas cleaning

The synthesis gas passes through a water quench, acidic scrubber, alkaline scrubber, glycerin scrubber for fine dust removal, desulphurisation and gas drying stages.

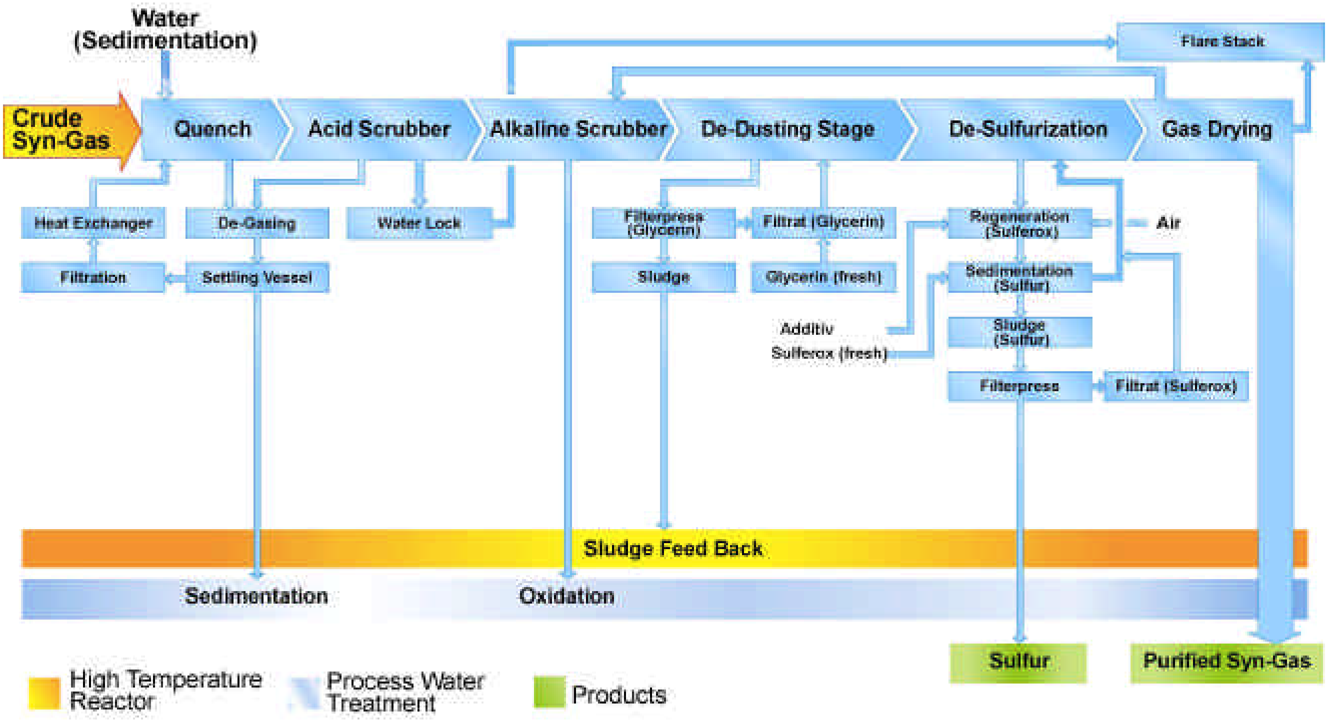
Firstly the crude synthesis gas exits the reactor at approximately 1200°C and flows into a water jet quench where it is cooled almost instantaneously to about 70°C. The shock-like cooling avoids the formation of dioxins, furans and other organic compounds from elementary molecules in the syngas due to the de novo Synthesis back reactions. De novo synthesis reactions are known to occur in waste heat boilers where a slow cooling in the range from 400°C to 250°C of flue gases with chlorine compounds, uncombusted organic molecules and catalysts such as dust will result in dioxin formation.



Measurements have proven that this is avoided in the THERMOSELECT process. Entrained particles such as graphite and mineral dusts are also separated out in the quench.

The gas path is connected to a water lock tank serving as a safety pressure relief device. In case of a sudden pressure rise above 500 mbar in the gasifier, for example due to a propane bottle burst, the synthesis gas is relieved to the safety flare where it is combusted.

Following the quench the synthesis gas flows through an acidic scrubber where further HCl and HF acids are removed. The acid content of the gas depresses the flushing liquid of these scrubbers to pH~3 which results in the volatilized heavy metals and their compounds dissolving as metal ions. Weaker acid formers such as H_2S, SO_2, and CO_2 do not dissolve at this pH value.



The acid scrubber is followed by an alkaline scrubber which uses NaOH in solution to knock out any residual acid liquid droplets.

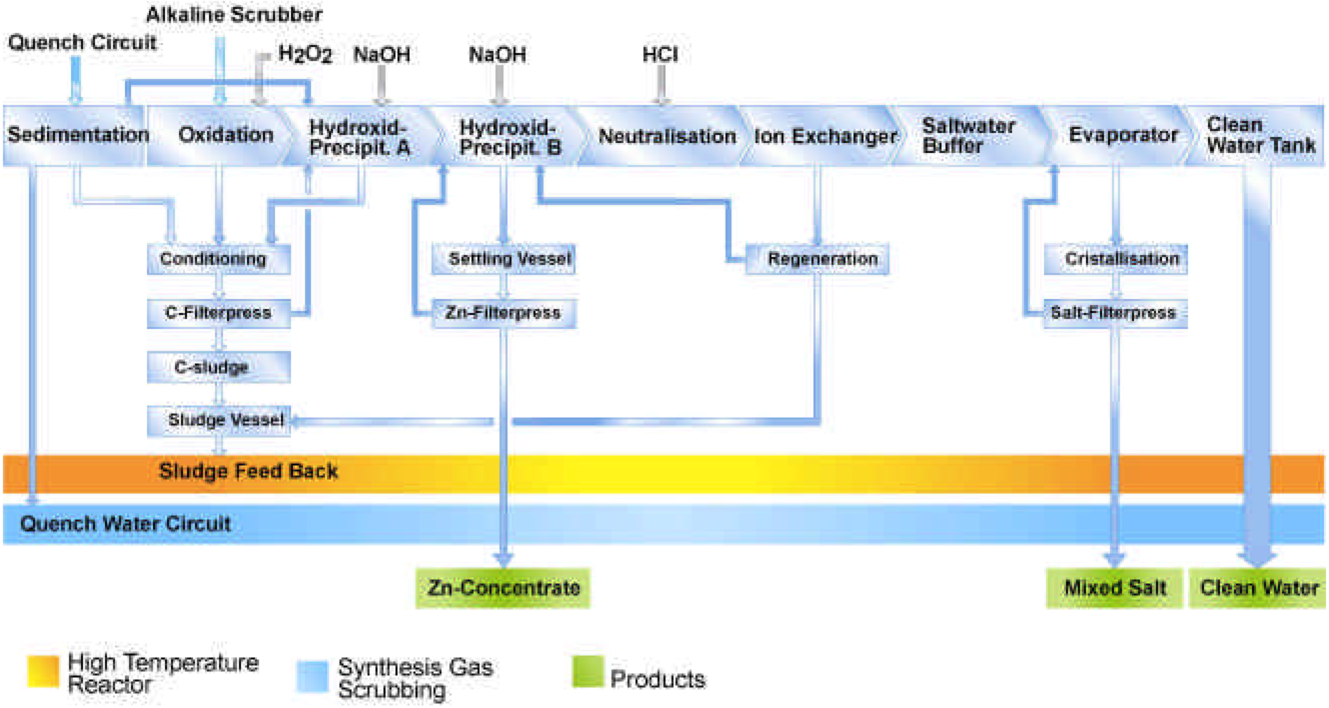
The alkaline scrubber is followed by a glycerin scrubber for fine dust removal. The glycerin reduces the surface tension of the liquid which enhances the capture of very fine residual dust particles from the synthesis gas. The water/glycerin/solids solution is transferred to a filter press were the solids are separated out. The solids are transferred back into the high temperature reactor.

The synthesis gas is then passed through a desulphurisation process. The scrubbing liquid contains an Fe-III complex (Sulferox) which is used to remove the H_2S from the gas. The process allows the conversion of the H_2S into elemental sulfur. The process is a redox-process in which the H_2S is oxidized to elemental sulfur and water by the conversion of the Fe-III into a sulfur Fe-II complex. This conversion process takes place within the Sulferox scrubber. In a regeneration unit, the scrubbing liquid is then oxidized by blowing air through it which converts the Fe-II back into the Fe-III complex. Elemental sulfur precipitates during this stage which is removed from the liquid by means of a filter press system.

Following desulphurisation, the dew point of the gas is lowered by direct contact with cold water in a gas drying scrubber. The lowering of the gas dew point prevents condensation in downstream equipment such as the power generation infrastructure and also removes residual traces of vaporized heavy metals.

Process water treatment

The process water originates from the condensed water vapour inherent in the processed waste and from the reaction products of the gasification process. Other small process water streams are generated from the gas scrubbing processes. The water treatment process occurs in batches which is a reflection of the relatively small quantity of water undergoing treatment.
The water from the quench circuit is settled, solids are removed and returned back into the high temperature reactor.



The water from the alkaline scrubber, with traces of hydrogen sulfide dissolved in it, is fed into vessels and oxidized using hydrogen peroxide. Soluble sulfate is formed and prevents the evolution of H_2S gas in later processing stages. Also Fe-II is converted to Fe-III which assists in subsequent precipitation steps.
A two stage precipitation then takes place. In the first stage NaOH is added to raise the pH to about 5.5. At this point aluminum and iron hydroxides precipitate which are settled out with the aid of a polyelectrolyte. The sludge is captured and dewatered in a filter press operation. The solids are returned to the high temperature reactor.
In the second precipitation stage the pH is raised to about 9 through the addition of NaOH. This causes heavy metals such as zinc to precipitate as a hydroxide, which together with the addition of polyelectolyte is settled out. The resultant sludge is dewatered by a separate filter press. The resultant cake is a product of the process.
The next process is a neutralization step in which the pH of the water is reduced to 7 with the addition of HCl acid.
Thereafter the water is passed through an ion exchange unit. The ion exchanger reduces any residual concentrations of multi-valent ions such as calcium, zinc and traces of other heavy metals. The metal ions are exchanged for sodium ions. The regenerate from the ion exchanger is returned to the first precipitation step. The increased concentration of ions in the regenerate will allow capture of these residual ions in the subsequent precipitation processes.

In the final step the process water is passed through a two stage evaporation unit. Condensing clean water is reused in the plant. The remaining salt is extracted by a filter press and is a product of the process.

Ancillary units

An air separation unit supplies oxygen, nitrogen and compressed air. Oxygen is required as the gasification medium and is in a pure form to manufacture high quality products. Nitrogen is used for atmosphere inertisation during maintenance and compressed air is required for control equipment.
The mineral and metal granulate is stored in a bunker storage. The bunker is equipped with a loading crane.

There are multiple end uses for the purified synthesis gas:

- Hydrocarbon production e.g. Petrol
- Hydrogen (and Carbon monoxide in SOFC) e.g. Fuel cells
- Ammonia production e.g. Fertilizers
- Methanol manufacture e.g. Chemical industry
- Electricity e.g. gas engines, steam boiler and turbine and combined cycle options, gas turbines

The choice of power generating equipment is dependent on the price of power. Higher power generating efficiency processes would need to be supported by higher electricity prices.

TECHNOLOGY MATURITY

The THERMOSELECT Resources Recovery Facility process has been one of the most exhaustively assessed processes in the world. All assessments have been carried out by 10 independent Government audit authorities from Germany, Switzerland and Italy including the German TÜV (Technischer Überwachungs-Verein) and several Universities. A wealth of information exists on the process, documented in books and International Journal papers. This extensive independent evaluation process has been undertaken primarily to satisfy community and government perceptions on emerging technologies. THERMOSELECT has shown that combined gasification and smelting of the inorganic fractions of waste is a desirable alternative to incineration since it does not create dioxin contaminated dusts, ash, slag and flue gases.
An independent audit of emerging technologies revolving around pyrolysis and gasification has been undertaken by Juniper Consultancy Services Ltd. (Sheppards Mill, Uley, Gloucestershire, GL11 5SP, England) in January 2000, culminating in the report “Pyrolysis and Gasification of Waste, A Worldwide Technology & Business Review”. Over 100 companies were identified that are developing pyrolysis/gasification technologies. The report identified THERMOSELECT as the leader in the field in commercializing the technology for MSW and that has been able to account for all elements of emissions and the quality of products.

INPUT QUALITY & QUANTITY FLEXIBILITY

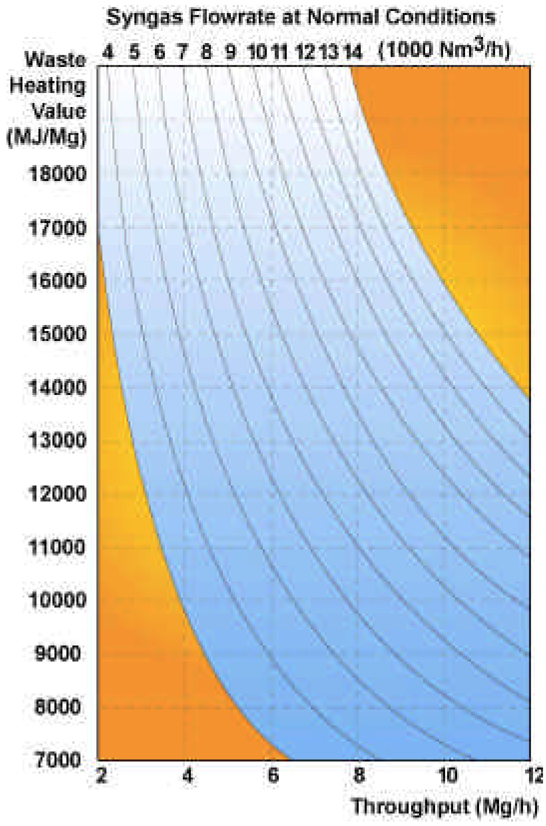
The chemical composition (ultimate and proximate analysis) of the waste will determine the quality and amount of raw synthesis gas. This in turn will determine the extent of gas refining required. It has been shown that the automated nature of the THERMOSELECT process adjusts itself to any deviations in waste quality (for example water content). Also, within reason, the quality of the products produced has been shown to vary very little as the waste source is changed from one to another.

One significant advantage of the THERMOSELECT process is its flexibility to handle raw as received waste of various kinds. Large bulky items (e.g. furniture) may be shredded and tipped into the bunker.

Liquid wastes such as sewage sludge etc. can also be processed. They are metered into the high temperature reactor together with the recycle streams into the transition section between the degassing channel and the reactor.

The process can also treat industrial wastes. The Chiba plant in Japan has been specially configured for this.

The capacity range of a standard thermal train is depicted right-hand as function of waste heating value. The upper bound of the process is the capacity of the gas scrubbing and process water treatment equipment, whereas below the lower bound the consumption of secondary fuel becomes excessive.



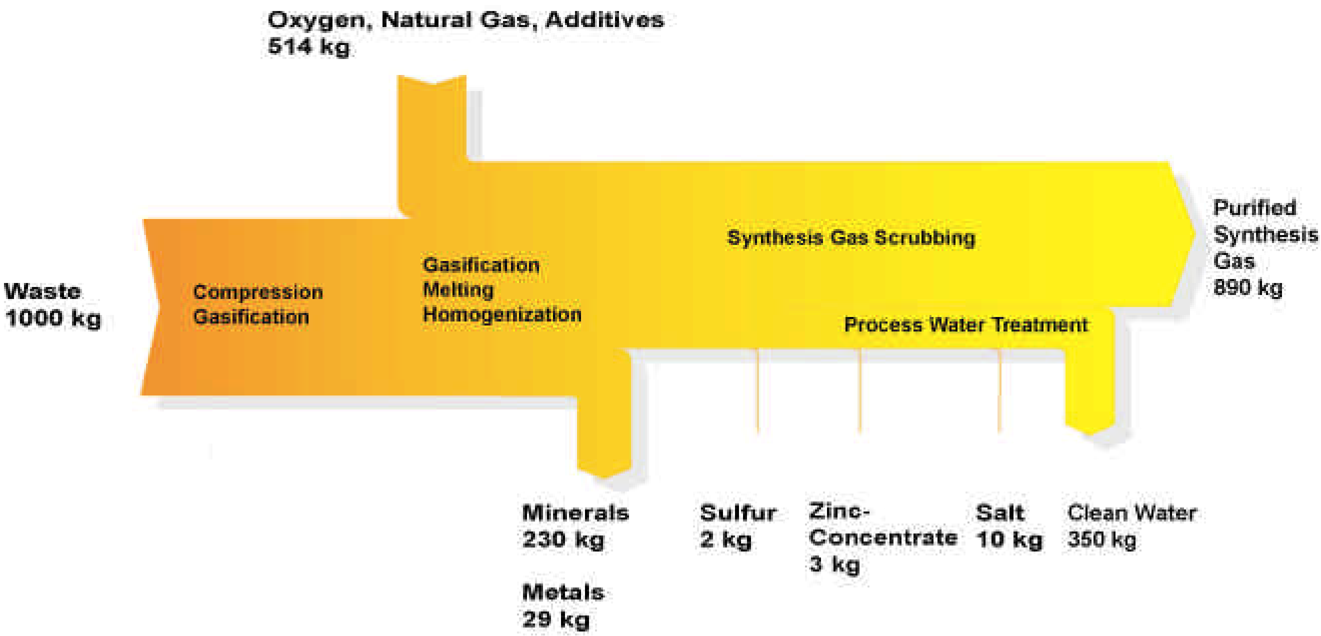
ENVIRONMENTAL ISSUES

Resource Conservation

The THERMOSELECT Resource Recovery Facility was conceived as a means to recover the maximum possible benefit out of mixed wastes that cannot be economically recycled. The process is for the continuous processing of mixed wastes with the primary goal of achieving the highest possible yield of high quality recyclable products at the lowest possible ecological pollution level, with simultaneous utilisation of the chemical energy contained in the waste.

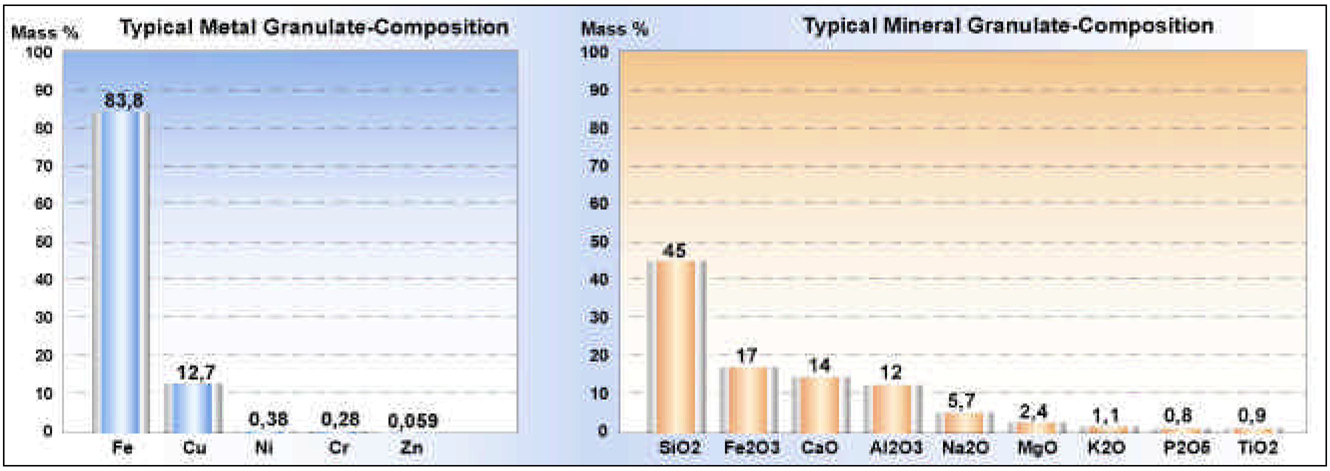
The products that are manufactured together with their reuse potential are:

- Mineral granulate reused as gravel substitute in concrete, as shot blast or as road base
- Metal granulate recycled into the metal industry
- Sulfur reused in the sulfuric acid and fertilizer industry
- Zinc concentrate reused in the zinc smelting industry
- Salt reused in the chlorine manufacturing industry
- Water reused in the process
- Synthesis gas either converted to further chemicals or power



Solid Residues

Unlike other pyrolysis/gasification processes THERMOSELECT does not produce any chars or oils or ashes which need subsequent disposal.
The mineral granulate is a completely inert glassy granulate that has been molten down at high temperature (>1600°C). The leachability of the mineral granulate is negligible and a typical composition is shown below.

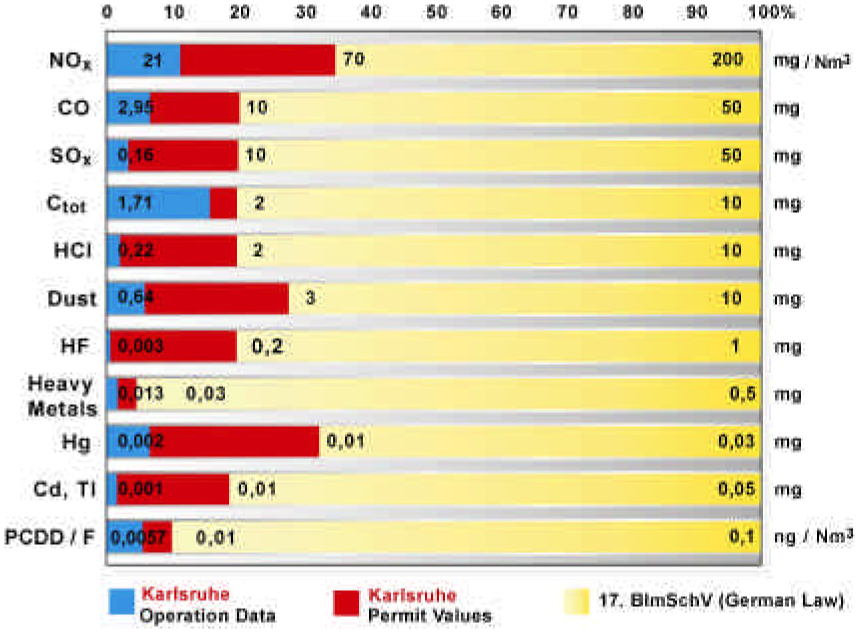


The metal granulate is a iron – copper alloy which is reusable in the metals industry.
The Karlsruhe experience has shown that it is possible to reuse the entire above product range within a relevant industry.

Air and Water Emissions

There are no water emissions from the process. The water in the waste is purified to drinking water quality and is reused in the process as cooling tower make up.
Air is extracted from the waste receival and bunker areas and routed through a small bag filter for dust removal followed by a UV lamp unit which oxidizes any odors.

Other emissions to air are the exhaust gases from the unit that converts the synthesis gas into power. These emissions have been extensively tested in Karlsruhe and are monitored continuously (CEM) for compliance. The following figure indicates emission levels obtained in the Karlsruhe plant.
The diagram shows the most stringent emission limits in the world are the German Law (17. BImSchV- yellow bars).
THERMOSELECT have undertaken to achieve at least 70% lower emission values than the current law (permit values as red bars). The actual measured emission values achieved are lower than the permitted values (blue bars). No other thermal technology treating waste in the world today can achieve such low gas emission levels at competitive conditions.
THERMOSELECT are currently setting the standards for Best Available Technology.



PREVIOUS EXPERIENCE AND CURRENT PROJECTS

Chiba / Japan


Karlsruhe / Germany

Fondotoce, Italy.

Plant Capacity: Single line, 32000 t/a
Operation: Demonstration plant in operation from 1992 to 1998
Synthesis gas utilisation: Gas motor power generation

Karlsruhe, Germany.

Plant Capacity: 3 lines, 225 000 t/a
Operation: 1999
Synthesis gas utilisation: Steam turbine power and district heating

Chiba, Japan, Kawasaki Steel licensee.

Plant Capacity: Two lines, 100000 t/a (MSW and industrial wastes)
Operation: September 1999
Synthesis gas utilisation: As fuel in Chiba Works

Ansbach, Germany.

Plant Capacity: One line, 75000 t/a
Operation: Under construction, Startup in 2002
Synthesis gas utilisation: Gas motor power generation

Hanau, Germany.

Plant Capacity: Two lines, 90000 t/a
Operation: Permit granted February 2000. startup 2004.
Synthesis gas utilisation: Steam turbine power generation

Giubiasco, Switzerland.

Plant Capacity: Two lines, 150000 t/a
Operation: Concession Arbitration Procedure pending, startup in 2003.
Synthesis gas utilisation: Steam turbine power generation

Herten, Germany.

Plant Capacity: Three lines, 225000 t/a
Operation: Permit request phase, startup 2004.
Synthesis gas utilisation: Steam turbine power generation

Mitsubishi Materials Mutsu, Japan - Kawasaki Steel sub-licensee

Plant Capacity: Two lines, 50000 t/a
Operation: Firm Order received
Synthesis gas utilisation: Gas motor power generation

Other licensees: Daewoo, South Korea