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Utilizing plasma technology for chemical reactions in controlled atmosphere

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Abstract - In recent years ScanArc Plasma Technologies AB has completed several successful development programs utilizing the outstanding properties of plasma technology for chemical reactions in controlled atmosphere of both organic and inorganic compounds. It is possible to choose either reducing or oxidizing conditions whichever is most suitable for the material to be processed and the chemical reaction since the plasma represents an independently controlled energy source. This new development of plasma technology for improving the environment has been used to successfully demonstrate the following applications on a pilot plant scale.

- Complete decomposition of chlorinated hydrocarbons, including PCB.
- Decomposition of compounds containing NO_3, NH_x or CN groups without incurring NO_x.
- Reduction and recirculation of organic iodine in an incinerator.
- Destruction of municipal waste material or refuse derived fuels by conversion into non-hazardous fuel gas and a non-leachable slag.
- Destruction of SPL from the aluminium industry.
- Selective reduction of metal oxides in a slag reduction furnace.

1. INTRODUCTION

A common feature of conventional chemical processes is that the generation of heat is closely connected with the chemistry of the reactions occurring. However, applying reaction heat with plasma generators renders it possible to control heat input and chemical environment independently. For instance, it is possible to heat a reducing gas to high temperature without introduction of oxygen or, oxygen can be heated without introduction of any fuel.

In the ScanArc pilot plant several new processes have been tested and demonstrated, mainly based on the application of plasma heating to create high temperature reducing conditions. Process testing in the pilot plant is made at power levels ranging from 200 kW (for hazardous waste destruction) to 2 MW (for metallurgical applications). Test duration varies from a couple of hours to continuous operation during one week.

The processes presented in this paper are used to decompose various compounds either for the destruction of hazardous material or for the recycling of metals. Recently several plasma processes for waste destruction have been presented (1-3). The Plasmadust process for recovery of metals from stainless steel making baghouse dust, commercially operated by Scandust AB in Sweden, has been described elsewhere and will not be dealt with in this paper (4-7).

2. DECOMPOSITION OF HAZARDOUS WASTE

Organochlorine products constitute a threat to the environment since their decomposition can produce toxic products among which polychlorinated dibenzo-p-dioxins (PCDD), are the most known and most toxic groups (2). If however the PCDD are heated to high temperature it will decompose into simple molecules or atoms as hydrogen, carbon monoxide, carbon and hydrochloric acid. Although theoretically simple, the very dangerous nature of the compounds renders it necessary to obtain an extremely low residue content of PCDD in the off-gas. By using a plasma gas to heat the waste material and the high exit velocity from the plasma generator for mixing of the plasma gas and the waste stream, complete decomposition can be guaranteed. To limit the production of nitrogen oxides due to the high combustion temperature necessary for decomposition, the oxygen potential is controlled.

The ScanArc process for decomposition of hazardous waste shown in figure 1 is made up of three stages. In the first stage air is heated together with some carbon or hydrocarbons in a non-transferred type plasma generator. The air to fuel ratio is controlled so that the carbon dioxide content is less than 25% of the carbon monoxide content in the produced gas. This will limit the content of nitrogen oxides (NOx) to less than 50 ppm, as shown in Figure 2, which shows the results of thermodynamic calculations considering the following reactions:

$$N_2 + O_2 = 2\,NO$$
$$2\,N_2 + O_2 = 2\,N_2O$$
$$N_2 + 2\,O_2 = 2\,NO_2$$

for the formation of NOx, when the partial pressure of oxygen is set by the equilibrium:

$$CO + O_2 = CO_2$$

In a second stage the hot reduction gas is introduced to a reaction chamber together with the material to be decomposed. Secondary air (or hydrocarbons) is added to obtain desired carbon monoxide to carbon dioxide ratio. In a third stage a venturi scrubber will clean the produced fuel gas.

PCB oil with 35% Cl has been treated in our pilot plant. The plasma generator was operated at 300 kW. The air flow rate to the plasma generator was 70 m^3(n)/h and the LPG flow 6 m^3(n)/h. We introduced PCB oil at a flow rate of 300 dm^3/h. Sampling and analysis of the produced fuel gas showed contents of dioxin (TCDD equivalent, a weighed value according to toxic effect) of less than 0.2 10^{-9} g/m^3(n) and contents of NO_x less than 100 ppm.

By the same method nitrate and amino containing compounds (by-products from production of explosives) were treated. In this case hydrocarbons were added to the reaction chamber to control the CO_2 content and to keep the NO_x in the fuel gas within acceptable limits. A NO_x content below 100 ppm was obtained.

Another application of the ScanArc process for decomposition under controlled atmosphere that has been tested is the recovery of iodine from organic iodine compounds. In this case $Na_2S_2O_4$ was added to the scrubber water for recovery of the produced iodine. In preliminary tests good recovery rates have been obtained. The tests were made in a commercial size reactor vessel with an installed plasma power of 1.5 MW and a capacity of 1 ton per hour. A longer test series will be performed later this year to optimize the process.

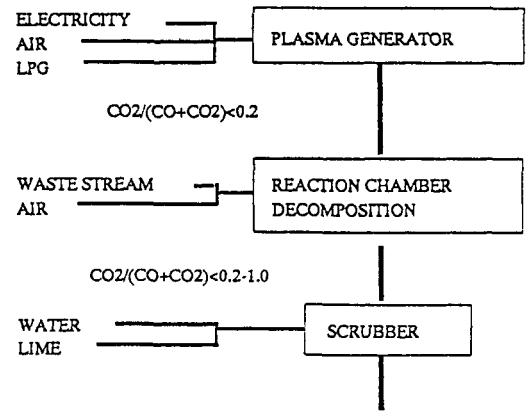

Figure 1 The ScanArc Process for Decomposition of Hazardous Waste.

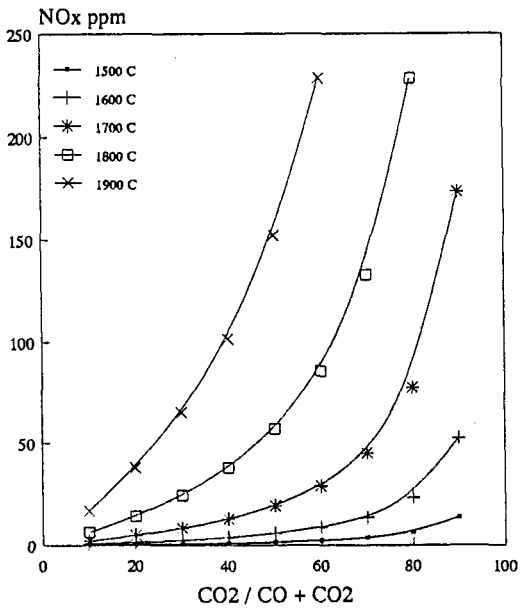

Figure 2 NOx formation as a Function of Degree of Post Combustion and Temperature.

3. DESTRUCTION OF SOLID WASTE

Solid waste material such as municipal solid waste (MSW) or various refuse derived fuels (RDF) can be gasified to produce a fuel gas. The pyrolysis will produce a gas containing various hydrocarbons including dioxin. By heating the gas in a controlled atmosphere the hydrocarbons can be decomposed to simple atoms and molecules.

In the ScanArc process for destruction of solid waste, the PLASMAWASTE process, which is shown in figure 3, the solid waste is gasified in a shaft gasifier by introduction of preheated air. Inert material will melt and will be tapped as non leachable slag. The resulting gas containing tar and hydrocarbons is treated by heating and partial combustion by a plasma heated air stream. Sulphur can be removed from the hot gas (1200°C) by introducing the gas into a shaft filled with dolomite where the sulphur in the gas, mainly H_2S, will be absorbed. The hot fuel gas is then partly used to preheat the air before it is fed to the gasification shaft.

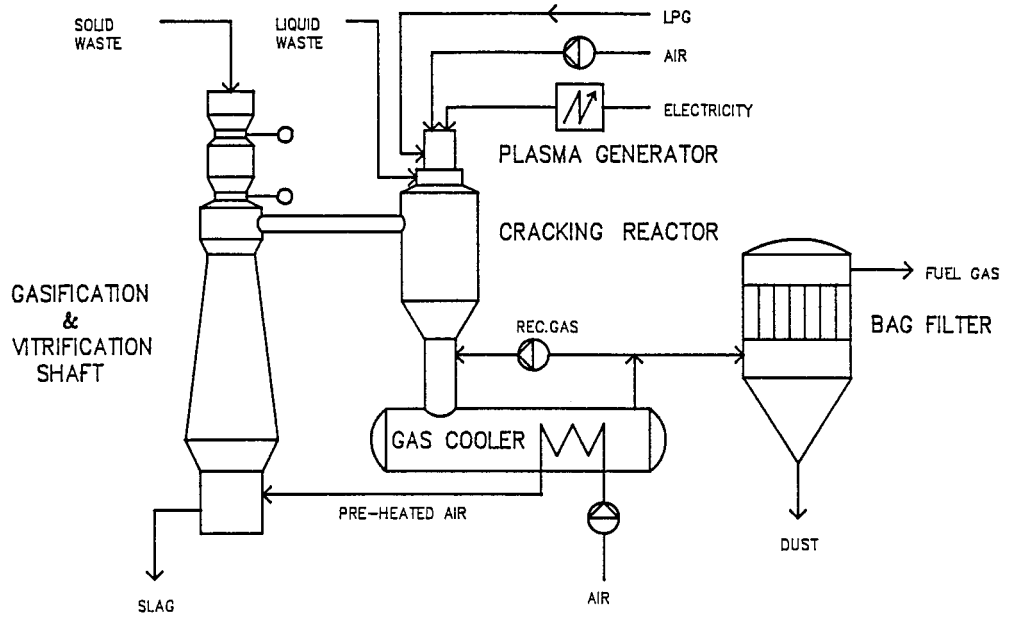

Figure 3 The PLASMAWASTE Process - Flow Sheet

Tests have been made with ordinary (MSW) municipal solid waste and with (RDF) refuse derived fuels from car shredding. The tests have been focused on minimizing production of chlorinated hydrocarbons (such as dioxin) and to obtain a non leachable slag. In both areas we have obtained excellent results. The dioxin content in the produced gas was lower than $0.1*10^{-9}$ g/m^3(n) and the analysis of the water from leaching tests of the slag was well within 6 times drinking water standard.

4. DESTRUCTION OF SPENT REFRACTORIES

Refractories used in the furnace for aluminium production have to be replaced after some time. The spent refractories contain cyanide and fluorine as well as carbon and represents an environmental problem.

ScanArc has also developed and demonstrated a process, which is shown in figure 4, in which the spent refractories are heated, partly oxidized and melted in a plasma heated reactor. The cyanide will decompose and the fluorine will leave as hydrogen fluoride. In a venturi scrubber the hydrogen fluoride is reacted with lime to form flourspar (CaF_2) or, alternatively, the gas is introduced in a shaft filled with aluminiumoxide which will absorb the fluorine for later recirculation to the aluminium process. A liquid slag is produced from the refractory material. The solidified slag is inert and can easily be deposed off. Alternatively, the oxygen potential of the slag can be lowered and the basicity raised to trap the fluorine in the slag for disposal.

A series of tests have been made in the pilot plant. The plasma power level was 1 MW for a feed rate of 1500 kg/h. Leaching tests according to EPA standard on the produced slag proved the slag to be very stable.

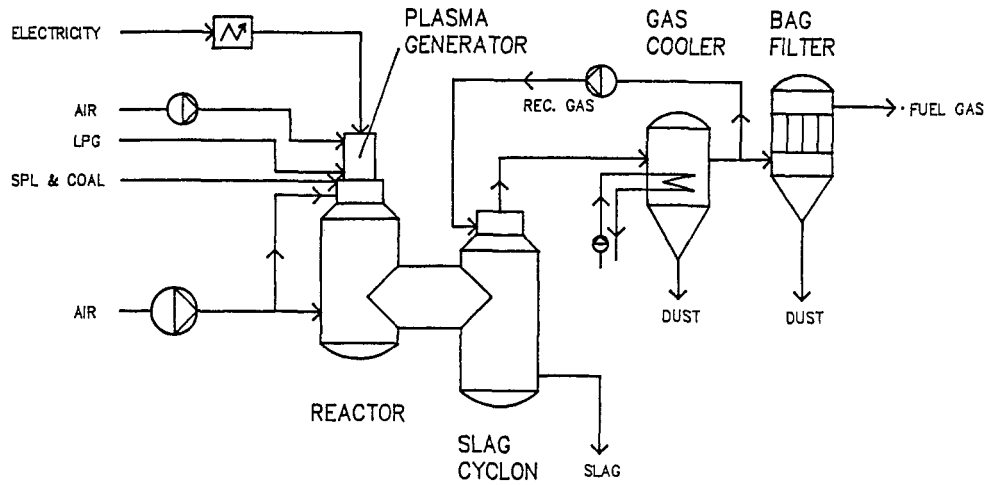

Figure 4 SPL Decomposition - Flow Sheet

5. SELECTIVE RECOVERY OF METALS

For the selective reduction of one or more metals from a mixture of metal oxides a new process has been developed and tested. An application of this new process is the treatment of secondary materials from zinc and lead production and the treatment of off-gas fumes from Electric Arc Furnace (EAF) scrap melting. The process is shown in figure 5.

In this new process the reaction takes place in a molten slag bath. The temperature of the gas is controlled by the introduction of plasma heated gas into the slag bath. By adjusting the composition of the gas, the oxygen potential and thus the reduction of the slag can be controlled.

The slag reducing furnace is lined with refractories in the bottom part where the produced metal phase is collected while a water cooled panel is used in the reaction zone. The panel will be covered with a slag layer.

The plasma generator delivers the heated gas into the slag bath which will give a vigorous stirring of the slag. The reducing agent, such as coal is fed into the slag bath and due to the vigorous stirring the reduction of the different metal oxides follows close to the equilibrium. Metals with a high vapor pressure such as lead and zinc will leave the furnace as metal vapor.

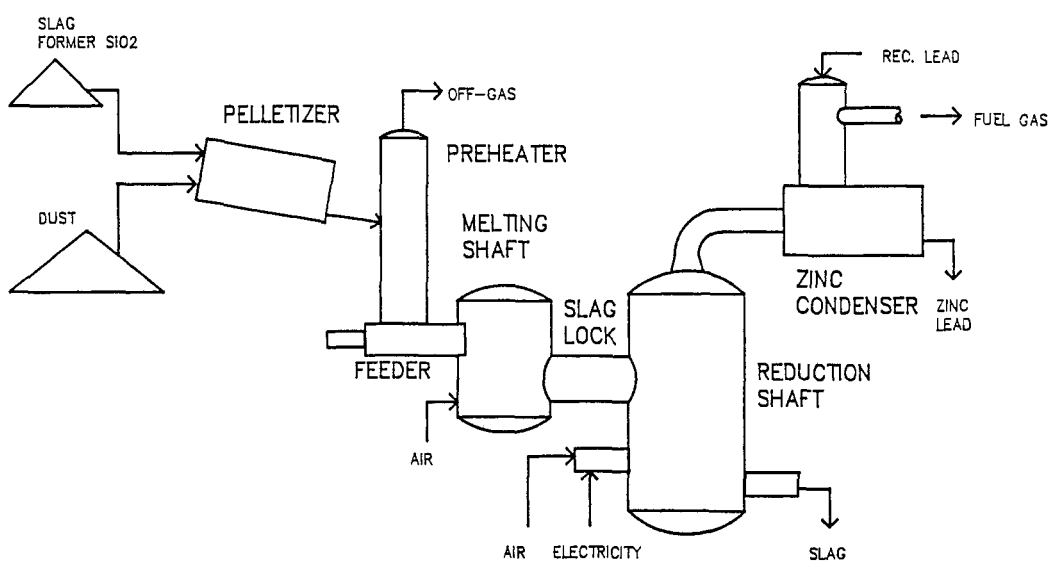

Figure 5 Dust Slag Reducer - Flow Sheet

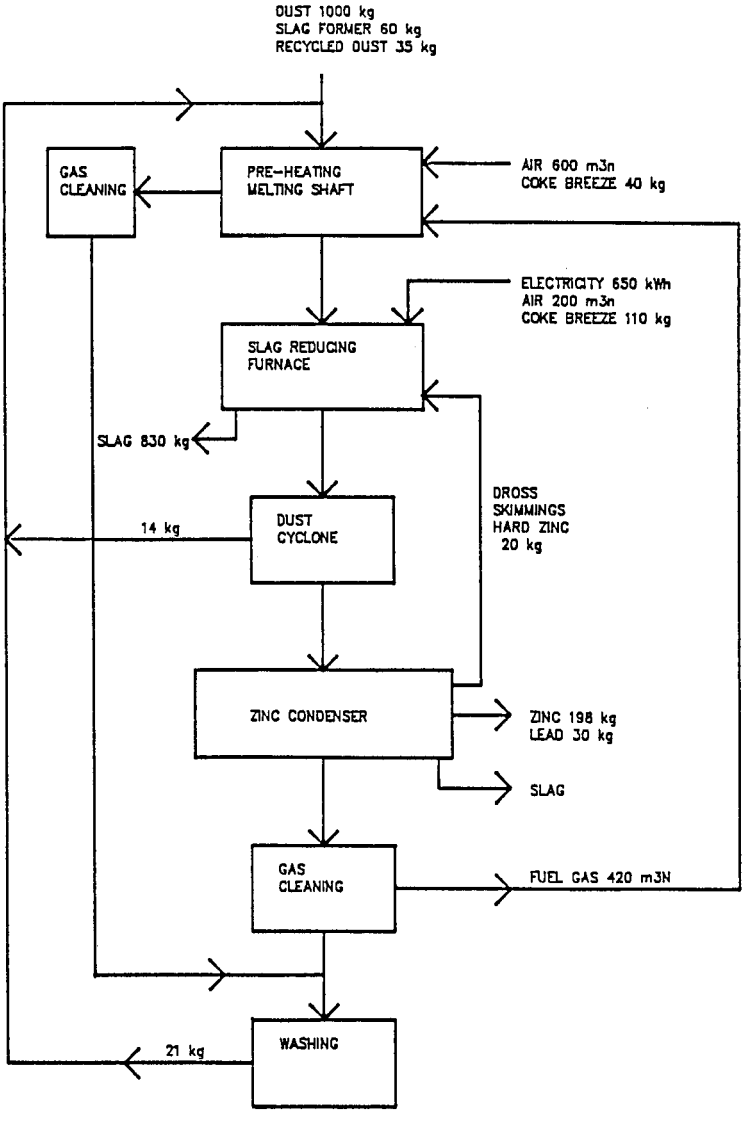

Figure 6 Dust Slag Reducer - Material Balance

The off-gases leaves the slag reducer at about 1300°C and has to be cooled and cleaned in order to separate the metal and metal oxide from the low calorific fuel gas. When processing EAF dust with a high content of evaporating metals, these metals can be condensed out of the off-gas in a zinc spray condenser. At lower contents of metal vapor, it may be more convenient to oxidize the metal vapor by burning of the off-gas and collect the metal oxides in a bag filter.

The slag reducer has been operated in the pilot plant on various feed materials testing different metallurgical reactions. In one case arc furnace baghouse dust was reduced. Two plasma generators were used, each operated at about 600 kW. The feed material contained 20% zinc, 1.5% lead and 35% iron. An example of a material balance for the dust slag reducer is given in figure 6. After the reduction the slag contained less than 0.1% zinc and lead while no iron was reduced to metal.

6. CONCLUSIONS

As has been described in this paper, the separation of heat input from chemical environment by use of plasma heating, opens many new opportunities for the chemical process engineer. Careful control of oxygen potential and temperature makes it possible to intensify certain reactions while other reactions are suppressed.

It has also been described that ScanArc has developed a versatile system for decomposition and destruction of hazardous waste material. The heart of the system is a plasma heated cracking reactor, used separately or coupled with a gasification shaft or slag cyclone. The very efficient and rapid decomposition of various organic and inorganic compounds depends mainly upon the good mixing conditions in this reactor.

ScanArc has also developed a process for recovery of metals using a slag reducing furnace. Plasma heated gas is delivered into a slag bath. By adjusting the enthalpy and composition of the gas, the temperature and oxygen potential can be controlled in the slag reducer. Due to vigorous stirring of the slag bath the reduction follows close to the equilibrium of reactions.

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