BATCH OPERATED GASIFICATION
AND OXIDATION PROCESS
FOR THE RECOVERY OF PRECIOUS METALS

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To overcome emission problems of small-scale batch operated combustion systems a new thermal treatment process was developed to incinerate small batches of residues containing precious metals. The thermal treatment of single batches is necessary to start the recycling of the precious metals and to refund the customers delivering the residues. The new process is divided in a pyrolysis and a subsequent oxidation step. With conventional control techniques it was not possible to operate the system reliably with all different types of residues. Fuzzy-logic controllers were combined with new O\textsubscript{2}/PIC sensors in order to control the gasification process and to optimize the afterburner for low NO\textsubscript{x} operation. The main focus was to maintain a constant release of volatiles during the pyrolysis process.

The emissions of the overall process were reduced considerably. Furthermore, as a result of reduced peak loads by direct control of the pyrolysis, the size of the flue gas treatment systems can be reduced for new plants. The developed control techniques are now ready for application with other batch operated thermal processes.

INTRODUCTION

The recycling process of precious metals has been carried out for more than 100 years. The incineration or ashing process, which is the subject of this contribution, is one important step of this recycling system (see Figure 1).

Small batch operated combustion systems are currently used in Germany to incinerate different types of residues of the precious metal industry (such as electronics, clothing, sludge, and polishing materials). This process is used in separation works to produce ash enriched with precious metals that are recovered afterwards by chemical process or by melting the ash. The ash is analyzed to refund the supplier of the residues.

These batch combustion systems suffer from high emissions of products of incomplete combustion (PIC) and PCDD/PCDF. Burning fuels that are not always suitable for the combustion in such facilities causes these high emissions.

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A high content of volatiles causes very high amounts of combustion gases during only half an hour of the 8-hour process. During this time of high load the combustion in the afterburner becomes incomplete and hydrocarbons are emitted. Due to the composition of the residues and the incomplete combustion, high amounts of PCDD/PCDF are formed in the system. Even with an optimized combustion process with advanced combustion control systems, it was not possible to keep the PCDD/PCDF emissions within acceptable limits.

This process and the plants traditionally used are quite similar to batch operated medical waste incineration facilities used in the United States and several European countries. These facilities and the related problems are described in U.S. Environmental Protection Agency (EPA) (1994). Dioxin emissions of batch operated municipal waste incineration facilities and their reduction are described in Sakai et al. (1992) and Tejima et al. (1993).

To solve the described problems, the Institute of Process Engineering and Power Plant Technology (IVD) cooperated with two industrial partners, a manufacturer of gasification plants and an end user of the technology. The aim of the project was to develop a new, energy-efficient, and clean combustion process capable of keeping the emissions within the limits of the waste incineration regulations for this type of process.

This paper will describe the old and the new process and compare the emissions of these processes to each other. The combined gasification and oxidation...
process of the new incineration system will be explained with special emphasis on the applied control techniques.

THE TRADITIONAL INCINERATION SYSTEM

A report of the incineration facilities traditionally used in separation works for processing residues containing precious metals was given at the IT3 conference 1996 in Savannah (Sakai et al., 1992).

Figure 2 shows a scheme of such a traditional incineration facility. In the incineration chamber (1) the residues are incinerated directly on a hearth plate made of stone. Three natural gas burners heat the chamber, and the hot gases leave the chamber via flue gas channels (3) designed to heat the hearth plate. In the secondary combustion chamber (4) a combustion temperature of a minimum of 800°C is maintained with an additional gas burner in order to destroy PIC leaving the incineration chamber.

An important problem that occurred at these facilities was the emission of PCDD/PCDF. PCDD/PCDF concentrations of up to 250 ng/m³ (@ 11% O₂) have been measured in the exhaust gas of such a facility. Detailed investigations carried out at IVD showed that there was a clear relationship between products of incomplete combustion (PIC) and PCDD/PCDF. In addition an influence of hydrochloric acid (HCl) and sulfur dioxide (SO₂) concentrations in the flue gas on PCDD/PCDF formation was shown. The results of the measurements (Baumbach and Berger, 1993) and the reconstruction of the facility (Berger et al., 1995) showed that without an advanced control and incineration technique the processing of different residues with different heating values always produces high emis-

![FIGURE 2 Scheme of the traditional incineration facility.](attachment:image)
sions of PIC (see Figure 3). This is the main problem and is due to the batch operation mode.

THE CONCEPT OF THE NEW PROCESS

The key problem of the traditional process is the batch incineration process cannot be controlled anymore once it is started. The combustion process is an exothermic process. The energy released intensifies the process of gasification of the fuel and the volatile hydrocarbon burn, again releasing energy. This is a self-accelerating process, hence the release of the volatiles happens within a very short time, resulting in a huge amount of combustion gases.

The new process is designed to offer a better control of the degasification process. As an alternative for combustion, pyrolysis is used to decompose the fuel. This process is endothermic; hence, the release of volatiles can be controlled by the energy input.

Thermo Gravimetric Analysis (TGA) studied the influence on the pyrolysis process by controlling the energy input. The same fuel was analyzed several times with different temperature gradients in an N₂-atmosphere. By heating up the fuel with a constant temperature gradient the mass loss for certain time steps was analyzed. To quantify the influence of the temperature gradient, the max mass loss ratio during every run was used. The results are shown in Figure 4.

The diagram shows that the decomposition of the fuel, miscanthus powder was used in this example, can be controlled directly by controlling the heat-up of the fuel. These analytical findings were used to design the new process and to de-
develop a suitable control system. A fuzzy logic control strategy was used to exploit the potential of this new gasification/oxidation process concept.

DESCRIPTION OF THE NEW FACILITY

The description focuses on the reactor itself, the secondary combustion chamber, and how the process of thermal decomposition of the different residues is carried out.

Design of the Pyrolysis/Oxidation Reactor

Figure 5 shows the reactor of the new process. Six drums, each containing a batch of residues, are mounted on a revolver like rig. The rig can be moved on a rail system into the reactor where it is turned by an electric motor. Once inserted in the reactor the reactor is closed and the heat-up procedure starts. The reactor is heated by a natural gas burner, which is operated with an excess air value of slightly below one. Thereby, a reducing reaction atmosphere is achieved in the reactor. The heating rate of the reactor can be controlled directly by the burner. Nevertheless, it cannot be switched off, as stopping the burner would change the reaction atmosphere in the reactor to oxidizing conditions.

After the completion of the pyrolysis process the mode of the reactor is switched from pyrolyzing to oxidizing. Air is injected via a tube system directly into the drums to burn the remaining char. Whereas the pyrolysis process has to be slowed down, the char burning or oxidation process has to be accelerated in order to adjust a constant utilization rate of the facility.
The gases leaving the reactor are burned in the secondary combustion chamber. A detailed description of the secondary combustion chamber and how it is controlled can be found further below.

**Design of the Secondary Combustion Chamber**

The secondary combustion chamber is divided into two parts, the pre-combustion chamber and the main combustion chamber. The vertically aligned combustion chambers force a change in the flow direction, thereby causing turbulent flow around the edge, and enhance the mixing in the combustion chamber. The pre-combustion chamber has a comparatively small diameter; hence, the gas velocity in this chamber is very high. This assures a good mixture of the combustion gases even with very low flue gas flow. Improved gas mixing is necessary, for example, during the oxidation mode when the flue gas flow is extremely low. The main combustion chamber assures the required combustion temperature and residence time.

There are two air injections and one flue gas recirculation installed. Secondary air and recirculated flue gas are injected in the pre-combustion chamber; tertiary air is injected in the main combustion chamber. Tertiary air is mainly used to cool the combustion chamber in order to keep the temperature below 950°C.
**Operation Mode**

The facility is operated in one- or two-shift mode. At the beginning of every shift the reactor is filled and closed. After some safety checks the gas burners are started and the reactor is heated up. During the heating period the pyrolysis of the residues takes place. When the reactor reaches its operation temperature of 550°C, the pyrolysis is almost complete. After some time the operation mode of the reactor is switched to oxidation mode and the char combustion takes place. The operator of the facility decides how long this oxidation period will last. The duration depends on the fuel; hence, for proper operation a well-experienced operator is required. After the oxidation period the reactor is cooled down to 250°C by injecting water and the drum rig can be removed.

The described process can be divided into four operational steps or phases; these terms will be used in further explanations:

- **heating phase**: start-up to 250°C reactor temperature
- **pyrolysis phase**: 250°C to 550°C reactor temperature and for a queue time of a minimum of forty-five minutes
- **oxidation phase**: operator-defined duration (minimum of two hours)
- **cooling phase**: cool-down of the reactor till 250°C.

**COMMISSIONING OF THE NEW INCINERATION FACILITY**

The new facility was commissioned in the year 1998. At this time the facility was controlled by a simple time-triggered PLC-based control system. After some mechanical problems with the transportation system for the rig, the system worked. Nevertheless, two important problems limited the capacity and the operability of the facility:

- The heating of the reactor was carried out with a constant temperature ratio. Fuels with high content of volatile matter caused malfunctions. Excess temperature and excess pressure occurred in the system, so that the facility had to be stopped several times.
- The oxidation phase took too much time and for some types of fuels the char was not burned completely. Furthermore, particles were blown out of the drum by the oxidation air. This caused an unacceptable loss of material.

As a consequence of these problems, a new control system for the pyrolysis process was developed. Furthermore, the design of the process drums and the operation mode during the oxidation phase was modified in accordance with the results of detailed investigations at a lab scale facility.
NEW FUZZY-BASED CONTROL SYSTEM FOR A MORE CONSTANT PYROLYSIS PHASE

Two control loops were designed to overcome the problems experienced during the commissioning phase. The pyrolysis controller directly controls the pyrolysis process by affecting the energy input into the reactor, in the endothermic pyrolysis process. The controller of the secondary combustion chamber modifies the operation mode of the afterburner in order to adapt it to the batch operation mode.

Pyrolysis Controller

Figure 6 shows a block diagram of the controller. A measurable variable for the control system is the rotation speed of the flue gas fan. This speed is directly proportionate to the flue gas quantity. More gasification products in the reactor yield higher flue gas flows. The pyrolysis controller is very simple. Its main purpose is the control of the temperature in the reactor. If the rotation speed of the fan exceeds a certain value during the heat-up of the chamber, the power of the burner is reduced in order to reduce the degassing of volatiles in the reactor. As the degassing normally happens at temperatures around 300°C, the controller works only a limited time during the overall process as a pyrolysis controller. Most of the time it is a simple temperature controller.

Controller of the Secondary Combustion Chamber

Figure 7 shows the block diagram of the second fuzzy controller developed within the project. This controller is much more complex. For such a multivari-
able control system, the fuzzy technology has clear advantages by means of the design and commissioning of the controller.

The controller uses the following input variables:

- LS2: Current-type zircon-based O\textsubscript{2} sensor
- KS1: This is a flue gas sensor that measures a sum variable of PIC. The sensor is a zircon-based sensor
- T: flue gas temperature of the combustion chamber
- rotation speed of the flue gas fan

The following output variables are controlled:

- BP: burner performance of the natural gas burner heating the secondary combustion chamber
- SA: flap controlling the secondary air
- TA: flap controlling the tertiary air (cooling air)
- FR: flap controlling the flue gas recirculated

Besides the main function of a combustion controller, the flue gas recirculation is of special use for the batch process. During the pyrolysis phase, gas with a fairly high heating value enters the secondary combustion chamber. Conventional controllers react with higher amounts of secondary or tertiary air, resulting in high air excess values and high exhaust gas flows. By displacing the tertiary air with cold flue gas, the air excess value is kept low and the peak load of the combustion chamber, the exhaust gas fan, and the flue gas cleaning is reduced.
Another important control feature for batch processes is the self-adopting LS2/KS1 sensor combination. The combustion controller includes an O₂-controller. The set point of this controller is continuously adapted to the actual burnout characteristic of the secondary combustion chamber. For a steady state operated combustion system this burnout characteristic is fairly constant. This is not the case at batch operated systems. Bad mixture of the combustion gases at low-flue gas flows or insufficient residence time at high-flue gas flows may require higher air excess values than other operation modes. Therefore, the set point of the O₂-controller has to be adjusted continuously in order to assure minimum oxygen content for highest efficiency and sufficient oxygen content for complete burnout of the combustion gases.

OPTIMIZATION OF THE OXIDATION PHASE

The optimization of the oxidation phase was investigated in detail in a lab scale facility. The findings of this investigation were transferred to the industrial scale facility.

Investigations at the Lab Scale Facility

Figure 8 shows the reactor used to investigate the process in lab scale. The test facility is electrically heated. The residues are processed in a single drum. The axis of the drum is hollow. During start up, N₂ is led through the axis into the drum to create an inert atmosphere. During the oxidation phase air or air enriched

![Figure 8](image-url)  
1) Gas inlet into the axis of the drum; 2) Nozzles for gas outlet from the axis into the drum; 3) Electrical heating of the drum; 4) Pressurized air to clean the filters at the drum outlet.
with O₂ is led through the axis into the drum. In Figure 8, four nozzles are shown, which are designed to distribute the gas in the drum.

The air distribution and the operation mode of the facility during the oxidation phase were varied during several tests in order to optimize the design and the operation mode. The following variations were tested:

1) Air distribution directly through holes in the drum axis — this is similar to the air distribution at the large-scale facility after commissioning. The drum rotates continuously.

2) Air distribution via the nozzles to the outer margin of the drum. The drum rotates continuously.

3) Interval run A: Same air distribution as 2). The drum is now only oscillated with an angle <180°; hence, the nozzles always point downward to the lower part of the drum where the ash is.

4) Interval run B: Same air distribution as 1). The drum is stopped for two minutes and only during this time is air injected into the drum. After stopping air injection and waiting for the dust to settle, the drum is turned two times to mix the ash.

5) Same operation mode as 2). Additionally, the air is enriched with oxygen to 40% oxygen content after fifteen minutes of pure air injection.

Figure 9 shows the results of these tests carried out with wood chips. For the different operation modes, the duration of the oxidation phase was varied. The mass

![Graph showing completion of oxidation with different duration oxidation periods and different oxidation modes.](image-url)

**FIGURE 9** Completion of the oxidation with different duration oxidation periods and different oxidation modes. (Fuel wood chips).
loss was measured by weighing the fuel and the remaining ash. 95% mass loss was defined to be a complete oxidation.

The time required to reach this complete oxidation is considerably different for the various oxidation modes. With the additional nozzles (2) the oxidation time was reduced by approximately 25% compared to the original mode with axial air injection (1). With the nozzles and an additionally optimized operation mode (3) the oxidation time was reduced by 50%. This is a remarkable improvement. Additional experiments with oxygen enrichment showed that a further reduction is possible. Nevertheless, as the operator was satisfied with the 50% reduction, this additional improvement was not investigated in detail. The manufacturer of the plant suggested operation mode 4; the objective was to reduce particulate matter loss by blowout of the drums. The results showed that this mode is not acceptable in terms of operation time.

**Optimization of the Industrial Scale Facility**

For the subsequent optimization of the industrial scale facility operation mode 3 was chosen and adopted to the industrial scale. A stainless steel grate was welded in every drum. The grate was connected to the oxidation air supply with an individually formed tube. The position of the grate and the form of the tube depend on the position of the drum on the rig. In a certain position of the rig, all grates have to be at the bottom of every drum. In this position air is injected for several minutes before the rig is turned to ensure mixing of the ash. During the turning of the rig no air is injected to avoid the loss of ash. The air is distributed under the grate and, therefore, has to flow through the ash. Figure 10 shows the changed design of the drum mounted at the lowest position of the rig. The operating experience of the industrial plant validated the good experience with this oxidation mode at the lab scale facility.

![FIGURE 10  Design modification of a reactor drum.](image-url)
RESULTS OF COMPARATIVE MEASUREMENTS 
AT THE INDUSTRIAL FACILITY

These comparative measurements have been carried out to quantify the improvements with and without the modifications described above. To investigate this, measurements with three different fuels have been carried out, operating the facility in three different modes:

- **R0**: Conventional operation with a time-triggered control system
- **RI**: Operation with a fuzzy pyrolysis controller
- **RII**: Operation with a pyrolysis controller and a controller for the secondary combustion chamber (→ combined controller)

The new controllers primarily affect the pyrolysis phase. To quantify the improvements of the oxidation process, the results found at the lab scale facility have been transferred directly.

**Improvement of Pyrolysis Process**

The most important goal of implementing new controllers was to harmonize the pyrolysis process. Figure 11 compares the volume flow of flue gas during the pyrolysis phase for the three different control modes. The considerable improvement with the combined controller RII shows that the new control system makes the flue gas stream more constant. With the new control system the layout of afterburner and the flue gas treatment (filter, fan, and stack) could be reduced by 40% in future plants.

Figure 12 shows that the air excess rate during the pyrolysis phase was reduced considerably. Whereas the pyrolysis controller alone did cause a slightly higher oxygen mean value, the combined pyrolysis/secondary combustion control-

![Figure 11: Maximum of the flue gas stream during the process.](image-url)
ler reduced the oxygen content by almost 30%. This improves the efficiency of the process by reducing energy losses through the flue gas and decreases the potential of dioxin formation via de-novo-Synthesis.

Beside these quantitative improvements, the reliability of the facility was improved. Without the new fuzzy controllers, the process had to be stopped frequently due to excess temperature or excess pressure in the secondary combustion chamber. With the improved control system, all fuels that were fed according to the layout of the plant (a maximum of 400 kg organic material) were processed properly without critical situations.

**Reduced Emissions of Gaseous Pollutants**

Although the emissions of the new gasification/oxidation plant were already within the emission limits valid for waste incineration with the first control system, a further improvement of the situation was achieved. The flue gas recirculation during the pyrolysis phase improved the situation by two means:

- The injection of cold flu gas in the primary combustion chamber reduced the temperatures in the chamber and, therefore, avoided thermal NO\textsubscript{x} formation
- The oxygen content in the primary combustion chamber was reduced considerably; hence, staged combustion conditions were established during operation period with huge amounts of pyrolysis gas. Hereby, the N-conversion of fuel-N to NO was reduced.

Figure 13 shows the considerable reduction of NO\textsubscript{x}-emissions by the new control system. Besides the average reduction, the reduction during the pyrolysis phase itself is even more important for the operator. With the new control systems, all half-hour mean values were kept below 400 mg/m\textsuperscript{3}, which is the emis-

![Average oxygen concentration in the exhaust gas during the pyrolysis phase.](image-url)
This was not the case with the conventional control system. Figure 14 shows that this NO\textsubscript{x}-reduction was reached without higher CO concentrations. This shows that the air staging did not reduce the burnout of the gases.

Besides this favorable reduction of flue gas concentrations, reducing the emitted flue gas quantity lessened all emissions of the process. The reduced spe-

![Figure 13](image1.png) **FIGURE 13** Average NO\textsubscript{x}-concentration in the exhaust gas.

![Figure 14](image2.png) **FIGURE 14** Average CO-concentration in the exhaust gas during the pyrolysis phase.

![Figure 15](image3.png) **FIGURE 15** Total amount of flue gas emitted per kg fuel during the entire incineration process.
specific (per kg fuel) flue gas amount is shown in Figure 15. This reduction of approximately 15% means that the emissions of all gaseous pollutants are reduced by an additional 15%.

**Improved Efficiency**

Whereas the efficiency is normally defined as useful energy output in relation to the energy input; the energy output of this process is not the key interest. Therefore, the processed quantity of the residues in relation to the energy input is the relevant figure for this process.

Based on the measurements with different controllers and on the lab scale experiments, the consumption of natural gas and electrical energy was calculated. Figure 16 shows the change in the natural gas consumption during the different operation phases induced by the optimization. Whereas the reduction of natural gas consumption during the pyrolysis phase is quite small, the influence of the reduced operation time during oxidation significantly effects the overall consumption of natural gas.

Figure 17 shows the change in the electricity consumption. The data was calculated by taking into account the most relevant electricity consumers in the plant. Again the optimization of the pyrolysis process by the new controllers did not influence the energy consumption significantly. Nevertheless, the reduced oxidation time did effect the electricity consumption significantly. The figures show that the reduction of process time is the most relevant measure for reducing the energy consumption of the process. Besides a further reduction of the oxidation period, the reduction of the pyrolysis period by developing a detection system that

![FIGURE 16] Change in the consumption of natural gas due to the optimization measures.
shows the end of the pyrolysis process is a possible way to achieve such a further reduction of process time.

COMPARISON OF THE EMISSIONS OF THE NEW AND TRADITIONAL INCINERATION FACILITIES

For this comparison, data of a traditional incineration facility were used, which was investigated in detail by the IVD. Installing a combustion controller and new burners optimized this facility; details are described in Berger et al. (1995). The following table compares the traditional facility (with and without improvement) with the new incineration facility fully optimized. Table 1 shows the average values of all measurements carried out at the corresponding facilities. Unfortunately, at the traditional facility NOx-measurements were carried out only after the improvements.

Looking on the emission concentrations of the unmodified traditional facility shows how important the improvement of the situation was. Nevertheless, CO and

<table>
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<th>Component</th>
<th>Traditional facility</th>
<th>Improved facility</th>
<th>New, optimized facility</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO in mg/m³</td>
<td>1732</td>
<td>8.19</td>
<td>12.8</td>
</tr>
<tr>
<td>TOC in mg/m³</td>
<td>321.7</td>
<td>5.44</td>
<td>&lt;2</td>
</tr>
<tr>
<td>NOx in mg/m³</td>
<td>n.a.</td>
<td>115.7</td>
<td>156.8</td>
</tr>
<tr>
<td>PCDD/PCDF in ngTE/m³</td>
<td>143.8</td>
<td>0.17</td>
<td>0.01</td>
</tr>
</tbody>
</table>

FIGURE 17  Change in the consumption of electricity due to the optimization measures.
TOC values show that with a new combustion controller the burnout of the gases can be improved considerably. Only TOC values improved to a further extent at the new facility. NO\textsubscript{x} emissions of the new facility are a little worse compared with the old facility. There are two possible reasons:

- The temperature in the afterburner of the traditional facility is not as high because the temperature controller is limited to a maximum of 800°C due to material reasons.
- The residues burned in the traditional facility are not exactly the same as the one investigated in the new facility. Therefore, the comparability of the values is limited.

The comparability of the PCDD/PCDF emissions is also limited as the operation mode of the flue gas treatment of the new facility is similar but not exactly the same as the one in the traditional facility. Nevertheless, the changes are in orders of magnitude; hence, the improvement is convincing.

CONCLUSIONS

Good control systems are for batch operated systems even more important than for continuously operated systems. Operating conditions and flue gas streams change considerably during the process; hence, an automatic adaptation of the process is more important than under stationary conditions.

Fuzzy logic is a suitable tool to implement such automatic control systems. Commissioning and optimization of fuzzy controllers is much easier than it is when applying sets of linear controllers for multivariable control problems. Applying such new technologies shows that emissions are not necessarily higher and reliability is not necessarily worse for batch operated facilities.

Beside these operational advantages, the design of new plants can be optimized by means of reduced size of flue gas treatment and, hereby, reduced investment and operational costs. Taking these advantages into account, such improved control systems pay back very quickly.

NOMENCLATURE

PIC Products of incomplete combustion
\text{NO}_x Nitrogen oxide (mg/m\textsuperscript{3})
TOC Total organic carbon (mg/m\textsuperscript{3})
CO Carbon monoxide (mg/m\textsuperscript{3})
PCDD/PCDF Polychlorinated dioxins and furans (ngTE/m\textsuperscript{3})
O₂ Oxygen (Volume %)
HCl Hydrochloric acid (mg/m³)
SO₂ Sulfur dioxide (mg/m³)
TE Toxic equivalents (of dioxins according to NATO/CCMS)
NG Natural gas

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References


