Engineering today, benefitting generations to come.

Building thermal waste treatment plants is our line of work and our passion. We function as partner for engineering services, supplier for key components, or general contractor for entire plants. From planning through construction and commissioning to service, our company’s specialists are in place to assist and advise our customers. As a family-owned company we look back on more than 80 years of tradition. The combustion lines we have equipped at sites all over the world number more than 700, including those joint-ventured with competent partner companies. Unceasing technological evolution, particularly with regard to resource conservation, is essential to all our endeavours.
1. Introduction

Thermal waste treatment using grate-based systems has gained worldwide acceptance as the preferred method for the sustainable treatment of waste. Key factors are not only the reduction of waste volume and mass and the destruction or separation of pollutants but also the efficient production and use of energy (electricity, district heating, process steam), compliant disposal and optimization of the quality of the combustion residues.

From a quality and quantity perspective, waste avoidance and waste recovery measures play a significant role in reducing the throughput of recyclables in thermal waste treatment. Nevertheless, in Germany, for example, it can be assumed that residual waste has an average metal content of 4% by weight. Consequently, the combustion residues bottom ash and fly ash contain substantial amounts of metals which are finite resources and whose primary production is associated with high power consumption. The most important metals include aluminium, copper, zinc, non-ferrous alloys, chromium-nickel steels and iron.

In conventional grate-based waste-to-energy plants bottom ash is removed from the furnace via a wet-type discharger filled with water. In combination with the recovery of raw materials from combustion residues, the dry discharge of bottom ash is becoming more and more important. Particularly in Switzerland, but also in several other countries, this process has generated a great deal of interest in the past few years. On the one hand, the discharge of classified dry bottom ash is economically viable due to effective metal separation, maximization of revenues from metal recovery (non-ferrous metals, above all),
reduction of disposal costs as a result of weight reduction, and associated lower transport costs. On the other hand, there are additional benefits due to the enhanced quality of the discharged dry bottom ash and simpler bottom ash handling in subsequent treatment, preparation and recovery processes.

2. Residues of thermal waste treatment

In the combustion process the carbon in the waste is almost completely oxidized, heat is released, and water evaporates. The inert ash content in the waste and the solids formed in the gas phase are discharged, together with added additives, as residues (Figure 1).

![Figure 1: Residues of thermal waste treatment](image)

Bottom ash is an extremely heterogeneous mixture whose composition is determined by the composition of the waste input. Approximately 200-250 kg of bottom ash are produced for every Mg of waste combusted in a waste-to-energy plant. The bottom ash comprises ash particles (sintered, melted), incompletely burned substances

![Figure 2: Composition of the bottom ash](image)

Recovery of Metals from Combustion Residues

(< 1 % by weight), metals (ferrous and non-ferrous) in various forms as well as materials such as glass, ceramics and stones which pass through the system but do not participate in the thermal processes in the furnace. Molten products composed of silicates occur in irregularly shaped lumps of up to 1 cm. When the bottom ash comes into contact with water, a pH value of approximately 12 is reached; various mineralogical reactions take place and salts which dissolve easily (chlorides, sulphates) form a solution. Due to its pozzolanic properties, wet bottom ash solidifies like cement. Figure 2 shows the composition of the bottom ash and the metal percentages that can be separated by mechanical treatment.

Bottom ash produced during thermal waste treatment accounts for the largest mass flow of waste input at approx. 20-25 % by weight. The ash is currently used as a building material, e.g. in road and landfill construction, or as a mining filler. Nevertheless, a large amount of ash is still deposited in landfills.

Fly ash takes the form of particles in the flue gas flow prior to the introduction of additives (e.g. CaCO₃) into the flue gas cleaning system. Fly ash discharged from the furnace is referred to as boiler ash when it is separated in the boiler and as filter ash when it is separated in the filters. Residues that accumulate after additives have been added are referred to as flue gas cleaning residues.

Waste-to-energy plants are characterized by the fact that the various pollutants in the waste are either thermally destroyed or concentrated in the fly ash. Approximately 12.5 kg of fly ash in the form of white/yellow to grey dust are produced per Mg of combusted waste. The fly ash contains heavy metals (such as cadmium, lead and zinc) and organic compounds (PCDD/F). Figure 3 shows the chemical composition of filter ash prior to the addition of additives. The heavy metal contents relate to the metal content of 13 % by weight of the overall composition of the filter ash.

Fly ash is extremely hygroscopic and therefore tends to agglomerate. Currently the fly ash is either recycled as mine backfill, used in underground landfills, or deposited on landfills following chemical/physical treatment.
3. Metal recovery from wet-discharged bottom ash

The bottom ash discharged by a wet-type discharger is processed in conventional bottom ash treatment facilities to achieve defined structural properties so that it can be re-used as a construction material. At the same time, ferrous and non-ferrous metals and unburned material are separated, and the material is classified and aged [8]. Figure 4 shows an example of conventional bottom ash treatment [1]. This form of treatment is state-of-the-art and is implemented on an industrial scale at many sites. The basic processing steps are comparable but very different treatment facilities and concepts are used.

Between 1996 and 2010 almost 2 million Mg of bottom ash were treated in the facility illustrated in Figure 4. Figure 5 shows the percentage content of ferrous and non-ferrous metals, mineral materials and recirculated unburned material.

The method described can be supplemented by further bottom ash processing steps comprising wet-mechanical stages or washing to achieve high-purity metal products with few contaminants [8].

Martin GmbH für Umwelt- und Energietechnik developed the SYNCOM-Plus process to enhance the quality of bottom ash [3, 4, 8]. The SYNCOM process, in which combustion air is enriched with oxygen, is followed by a downstream wet-mechanical treatment facility which produces a granulate. The fine fraction and the separated sludge are then reintroduced into the combustion system to further sinter and destroy organic compounds (Figure 6).

The fine fraction is separated from the screened granulate (> 2 mm) and exhibits optimal quality for downstream metal recovery. It can be used without restriction as a mineral construction material.
4. Metal recovery from dry-discharged bottom ash

4.1. Dry discharge process

In Switzerland two different processes for the dry discharge of bottom ash in waste-to-energy plants with Martin combustion systems have been implemented on an industrial scale [2].

Figure 5: Wet-discharged bottom ash recovery figures 1996-2010


Figure 6: SYNCOM-Plus process diagram
The KEZO dry bottom ash discharge system is used on two lines at the KEZO Hinwil waste-to-energy plant (CH), and an open system with numerous process functions has been developed. Following combustion, the dry bottom ash is discharged via an almost horizontal channel in which the dry bottom ash is conveyed by means of vibration motors (Figure 7).

![Figure 7: KEZO dry bottom ash discharge system](image)

The dry-discharged bottom ash is split into two material flows by means of screening:
- **Coarse fraction** (> 5 mm),
- **Fine fraction** (≤ 5 mm).

Metals are extracted from both dry fractions using appropriate separating processes.

The ram-type discharger in its original design (without water supply), a newly developed and patented air separator and a cyclone are used in the Martin dry bottom ash discharge system employed on the two lines of the SATOM Monthey waste-to-energy plant (CH) (Figure 8).

Three material flows are separated from the dry-discharged bottom ash by means of air and cyclone separation:
- **Coarse fraction** (> 1 mm),
- **Fine fraction** (≤ 1 mm),
- **Bottom ash dust** (≤ 100 µm).

The coarse fraction, in which almost all metals are present, undergoes appropriate separating processes in order to extract the metals. Due to its outstanding pozzolanic properties, the largely mineral fine fraction can be used untreated as a cement substitute; for the solidification of waste, for example. The small quantities of bottom ash dust that accumulate are returned to the combustion process with the overfire air but the dust can also be separated by means of appropriate filter systems and recycled together with the fine fraction.
Recovery of Metals from Combustion Residues

The mass-dependent separation of fine fraction through application of the air separation principle in the Martin dry bottom ash discharge system produces different qualitative and quantitative bottom ash fractions as compared to size- and shape-dependent separation by means of screening in the KEZO dry bottom ash discharge system. The Martin dry bottom ash discharge system produces a metal-free fine fraction (≤ 1 mm) and a coarse fraction (> 1 mm) that is enriched with metals. In the KEZO dry bottom ash discharge system the fine fraction (≤ 5 mm) has a high metal content that can be extracted by means of appropriate separating processes; the remaining metals are present in the coarse fraction (> 5 mm).

4.2. Treatment of dry-discharged bottom ash

In the SATOM Monthey waste-to-energy plant (CH) the coarse fraction (> 1 mm) is treated conventionally using magnetic scrap iron separation, screening and subsequent non-ferrous metal separation (2 eddy current separators). Conversion to an optimized dry bottom ash treatment facility is in progress.

At the KEZO Hinwil plant (CH) the Development Centre for Sustainable Management of Recyclable Waste and Resources (ZAR, www.zar-ch.ch) has already developed several processing steps for the treatment of bottom ash fractions obtained by dry discharge and has implemented them on an industrial scale (process name: thermo-re). These are deployed successfully to recover ferrous and, above all, non-ferrous metals. Use of this equipment in treatment facilities for bottom ash that originates from other waste-to-energy plants is already under consideration.
The dry-discharged bottom ash is processed in three continuously operating facilities for:

- coarse fraction treatment,
- fine fraction treatment,

At present, only the ferrous metals are magnetically separated from the coarse fraction. The process for further treatment of the coarse fraction of dry-discharged bottom ash is currently under development and is due to be implemented at the KEZO Hinwil site plant (CH) at the beginning of 2012.

Figure 9: Fine fraction treatment

Figure 10: Non-ferrous metal processing facility
The fine fraction treatment facility (Figure 9) at the KEZO Hinwil plant (CH) processes the dry fine fraction (in the 0.7-5.0 mm particle range) with a very high separation efficiency for non-ferrous metals of more than 90%.

The added value of the non-ferrous metals recovered from the fine fraction can be substantially increased by further processing the non-ferrous fraction to enrich certain metals. The non-ferrous metal processing facility illustrated in Figure 10 has been implemented on an industrial scale for this purpose.

4.3. Mass balances

Analyses of the dry-discharged bottom ash at the KEZO Hinwil plant (CH) reveal the mineral, ferrous and non-ferrous metal percentage contents shown in Figure 11. Approximately 20% of the dry-discharged bottom ash is treated using the processes currently implemented. There is significant further potential for the recovery of recyclables.

![Figure 11: Mass balance of dry-discharged bottom ash at the KEZO Hinwil plant (CH)](image)

The aluminium and copper content is substantial as referred to the corresponding fractions fine fraction, non-ferrous material and light non-ferrous / heavy non-ferrous metals (Figures 12+13). The further processing steps result in significant enrichment and optimal recovery of recyclables from the totality of available material.

5. Metal recovery from filter ash

In 10 waste-to-energy plants in Switzerland heavy metals are removed from the fly ash produced during the thermal treatment of waste by means of an acidic fly ash extraction process (FLUWA process). The washed fly ash is then recycled together with the bottom ash [7]. This allows recyclables to be returned to the substance cycle through selective processing of the resultant heavy metal containing filtrate. The FLUREC process (Figure 14) separates cadmium, lead and copper cementate and recovers zinc, a valuable metal present in high concentrations in the fly ash (Figure 3), as a high-purity metal. Organic substances remaining in the filter ash cake, from which the heavy metals have been stripped during the FLUWA process, can be returned to the combustion process for destruction [5, 7].
Figure 12: Aluminium content in fine fraction, non-ferrous material and light non-ferrous metals

Figure 13: Copper content in ore, fine fraction, non-ferrous material and heavy non-ferrous metals
In acidic fly ash extraction the acid in the quench water from the flue gas cleaning system mobilizes and strips the heavy metals contained in the fly ash. In a filtration stage the low-metal filter ash cake is separated from the filtrate phase with high heavy metal content.

Figure 15:
Schematic diagram of solvent extraction/zinc electrowinning
Sources:
The filtrate is the raw material for the subsequent specific separation and recovery of the heavy metals.

The metallically stripped impurities are separated out as cementate in a filtration unit. Due to the high lead load of approx. 50-70 % by weight, the cementate can be sent directly to a lead smelter for further use. The remaining heavy metals present are recovered in the lead production process at the smelter and are returned to the substance cycle. The zinc is separated from the pre-cleaned filtrate by means of selective solvent extraction, and is then enriched and recovered electrolytically as high-purity zinc (Zn > 99.99 %) (Figure 15).

The filter ash cake, which is free of heavy metals, is returned to the combustion process to destroy the organic substances in the fly ash, particularly dioxins and furans. Plant operation, raw and pure gas parameters, and the quality of the bottom ash produced are not impacted by recirculation.

6. Summary and outlook

The described technologies and processes for the recovery of metals from wet-discharged and dry-discharged bottom ash and from filter ash point to the key role that thermal waste treatment residues are able to play in the efficient conservation of resources.

It is primarily thermal treatment with dry discharge and subsequent processing of the bottom ash fractions (thermo-recycling/thermo-re) that enables waste-to-energy plants to justify their status as universal recyclers. In addition to recovery of the energy inherent in the waste, the treatment of dry-discharged bottom ash is an important contribution to compliance with raw material and climate policies and to the promotion of a closed substance cycle in general. Dry bottom ash discharge also increases CO₂ savings potential in waste incineration because metal recyclables (ferrous and non-ferrous metals) can easily be recovered and returned to the raw material cycle with low consumption of primary energy. Furthermore, dry bottom ash discharge represents a further step towards waste-free operation and after-care-free landfills.

Martin GmbH für Umwelt- und Energietechnik is ready and able to implement dry bottom ash discharge processes in new plants or to integrate them into existing Martin plants. Plants can be converted to dry discharge without the need for major modifications to the combustion system, boiler or flue gas cleaning system.

By also combining thermal waste treatment with the FLUREC process to recover metals from filter ash and return the filter ash cake to the combustion system, it is possible to achieve maximum metal recovery from combustion residues in closed, process-integrated cycles. Only recyclable bottom ash and metal fractions remain, and these can be returned to the raw material cycle.

International requirements relating to energy efficiency and materials recovery by means of thermo-recycling in thermal waste treatment using grate-based systems call for the continuing development and optimization of existing technologies and concepts. The waste industry, universities and research facilities are already working hard to develop optimized and innovative ways of protecting the climate and resources sustainably.

7. References


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