CHAPTER 17 - SEPARATION PROCESSES

During the last decade, operating standards for MSW incinerators have rapidly become more stringent and the technology has generally followed suit. Many countries also enacted new legislation to improve the quality of incinerator residues for reuse or disposal in landfills. As a result, ingenious technical processes have been developed, generally to solve single problems, e.g., Hg or PCDD/PCDF emissions, or the leachability of APC residues. Each process typically created new problems, and often new, more concentrated residue streams. Consequently, compliance with the total set of imposed licence restrictions now requires a series of highly complex technologies to be added onto the incineration process. In some instances, these strategies may create unwarranted expenditures, and need to be considered in the context of Best Available Technology Not Exceeding Excessive Cost (BATNEEC). In general, the baseline concept of BATNEEC processes requires more focus on adequate process control and in-plant treatment techniques, which are relatively simple and robust. It is only when these options fail that secondary treatment is warranted.

17.1 DEFINITION OF PROCESS

In relation to residue treatment, the term "separation" includes all the techniques which are applied either to:

1) separate mass streams of different origin and quality, or

2) isolate single species from special residue streams in order to improve the quality of the respective residue and/or to recover the respective species

Separation processes are not only necessary to minimise potential environmental impact, but they are often necessary to render the residues suitable for use with respect to technical or engineering criteria.

Based on the discussion of the physico-chemical processes which take place inside an incinerator (Chapter 8), the incineration process should be optimised toward both minimising emissions and residue quantity based on the following:

a) the grate siftings, grate ash, boiler ash, filter ash, and scrubber residues streams should be collected separately to apply the best disposal or treatment option appropriate to each streams characteristics

b) the grate or bottom ash must be inertised to the greatest extent possible to enable utilisation or simple disposal

c) unavoidable hazardous products of combustion must be concentrated in the least voluminous side-streams

d) all treatment process steps must be tested to ensure ecological benefits

e) the process design must weigh the benefits of the treatment against the costs involved

The recently issued German guidelines on residential waste (TA Siedlungsabfall) are based on these fundamentals (Bundesministerium, 1993). It enforces the strict separation of all single residue streams. Only residues which are treated with the same process (e.g. boiler and fly ashes) are allowed to be combined. This is a simple and cost-effective means to enhance treatment of the residues. These techniques include on-site isolation of mass streams and post-incineration treatment by screening, and magnetic and eddy current separation.

Physical separation methods have a limited effect on the ash quality since they are only able to isolate single components already present in the original mixture. They do not necessarily modify the chemical properties of the ash, but are capable of removing materials which are potentially detrimental to recycling the bulk of the material, i.e., as in the utilisation of bottom ash. Better separation efficiencies can be obtained by taking advantage of physico-chemical parameter changes for separation purposes, without feeding additional chemical agents into the system. These methods can be carefully directed to separate special compounds or classes of compounds, which may result in very pure and marketable products. For example, physical separation of ferrous metal and metallic aluminum can be easily achieved from bottom ash. Additional technologies have been proposed or are in use, ranging from washing salts out of bottom ash to the production of pure HCl from wet scrubbing solutions via distillation.

Chemical reactions alter the chemical state of the species in question in order to obtain specific removal at high efficiencies. Applied or proposed chemical separation processes include leaching procedures using special media or precipitation processes to produce hydroxides, sulphides, or sulphates. But these techniques generally require the addition of special chemical reagents.

According to the definition given above, electrochemical processes are distinctive in that they make use of both chemical and physico-chemical methods, but do not require the use of additional chemical reagents to produce a special material.

17.2 PHYSICAL SEPARATION TECHNIQUES

Physical techniques consist of simple separation and/or classification of residues, and in most cases are limited to treatment of bottom ash. Due to the relatively large mass stream, one of the most effective means to modify bottom ash quality is to implement simple technical solutions. The following provides an overview of both primary and secondary measures which can be employed to treat the ash.

17.2.1 On-site Separation

Bottom Ash

The use of proper combustion control measures to enhance the completeness of burnout not only acts to minimise the organic contaminant content of the bottom ash, but also acts to enhance the partitioning of elements into the different mass streams of an incinerator. Bottom ash normally consists of grate ash combined with the grate siftings and in many facilities with the boiler ash. The grate siftings may contain a certain amount of incompletely combusted material and thus increase the total carbon content of the bottom ash. Furthermore, they may carry substantial quantities of metallic Al, Pb and Cu which are of concern if the ash is destined for most utilisation applications. However, the data on the quality of grate siftings is limited and varied. The results from an older study indicated there was no substantial difference in total concentration between grate ash and grate siftings (Schneider, 1986;). Even different separation and washing procedures used on ash (performed at the Swiss incinerator 'Zurich KVA 1') resulted in no significant deterioration of bottom ash quality by the inclusion of grate siftings (BUVAL 1990). Conversely, the NITEP and WASTE Programs both reported significantly higher concentrations of Al, Pb and Cu in grate siftings compared to grate ash (Environment Canada, 1991; WASTE Program, 1992). Furthermore, it is a common experience for considerable amounts of metallic Al and Pb to be found "frozen" in the chutes and collection hoppers underneath the grates.

Based on operating experience and the latest data, there is sufficient justification to recommend separation of both residue streams and to feed the grate siftings back into the furnace to burn the remaining uncombusted material in the grate siftings. However, it is important to note that the metallic components, such as ferrous, Al, Cu and Pb, should be removed from the stream prior to reintroducing the uncombusted fraction back into the incinerator. This practice is being performed in a limited number of German facilities and is enforced by the new German regulation in cases where the grate siftings contain more than 3% of unburnt carbon (Bundesministerium, 1993).

In the boiler ashes, especially in the ashes generated in the economiser, mobile heavy metals are found as well as semi-volatile organics (see Chapter 8). Hence in many countries, separation of this mass stream from the bottom ash is enforced by regulations (e.g., Bundesministerium, 1993). The Swiss research program cited above also recommends the separation of boiler ashes from the grate ash (Buval, 1990). The recommended practice of separate collection of the ashes from the heat recovery system is also supported by data generated during a Swiss investigation which involved conducting the Swiss leaching test on bottom ash after step-wise separation of the boiler ash and grate siftings. The results indicated that the grate ash was much less soluble than the combined streams. Moreover, the leaching behaviour of the pure grate ash is comparable to that of natural building materials like basalt, quartz, and gravel under the same test conditions (Vehlow et al., 1992).

Fly Ash and APC Residues

Fly ash collected in the combustion chamber ("hot-side" fly ash) is characterised by very low concentrations of thermally mobile metals, which are still in the gas phase in this part of the incinerator (Environment Canada 1985 and 1988). Consequently, dedusting of the hot flue gases in the front part of the boiler at temperatures well above 500°C could potentially remove a high percentage of the inert material from the ash stream and thus reduce the quantity of ash collected further downstream. However, it has yet to be determined whether the quality, especially the leaching stability, of materials separated at high temperatures would permit mixing this material with bottom ash. Studies on the benefits of such a system would need to be conducted, especially in relation to the quality of bottom ash destined for application purposes. On the other hand, the separation of this fraction may be advantageous with respect to the formation of PCDD/PCDF in the boiler, which is highly dependent on the presence of particulate carbon in the fly ashes (see Chapter 8). The coarse hot-side fly ash fraction may contain the major proportion of carbon and its separation should result in lower levels of organohalogen compounds in the flue gas. It is speculated that the resulting increase in concentration of volatile trace metals, such as Cd, Zn, As, or Pb, in the fly ash and APC residues would be acceptable, since these residue streams already require special treatment prior to disposal (in most countries).

Investigations into the behaviour of volatile trace metals under the conditions of hot gas filtration have been conducted by modelling a boiler-integrated cyclone in an electrically heated bypass duct (Borchers, 1989). A substantial reduction in concentrations was noted for some highly volatile metals in high temperature cyclone dust compared to those in downstream fly ashes. For example, maintaining higher temperatures (750°C) in the hot cyclone dust reduced Cd by more than 70%, the Pb by more than 60%, and the Sn by approximately 55%. PCDD/PCDF concentrations in the cyclone dust were in the order of 12 - 15 ng/g (total), which is low compared to the PCDD/PCDF loading in fly ash. There is no full-scale application of such a technology. Although the integration of a cyclone into a boiler seems feasible, other problems may be encountered during steady state operation in that a number of components in fly ash, especially sulphates and phosphates, are sticky at high temperatures and tend to build up in layers on the surfaces of the unit (see Chapter 10). In addition to increasing the frequency of the conventional soot blowing cycles to prevent the gas channels from being closed off in relatively short period of time, this technology would probably require more frequent maintenance to remove the deposits formed via Fickian diffusion, diffusiophoresis and thermophoresis mechanisms.

Because fly ash collected downstream of the heat recovery system contains characteristically high levels of volatile trace metals and semi-volatile organic compounds, it is recommended that these be collected separately from the bottom ash, as is the case in most countries. In several instances, there are additional regulations requiring the separate collection and handling of fly ash from the APC residues. For example, in Germany the access to different categories of landfills is regulated by a new federal guideline on the basis of results of the German DEV S4 leaching test

(Bundesministerium, 1993). This guideline classifies raw fly ash and residues from dry/semi-dry APC systems differently. As a result, the APC residues have to be disposed in underground disposal sites, whereas fly ash, at least after treatment, can potentially be placed in less costly aboveground landfills. In this case, separation of coarse fly ash prior to a lime-injection system or spray-dryer may be economically effective, and consequently cyclones or ESP's have been installed prior to the APC system in some incinerator facilities.

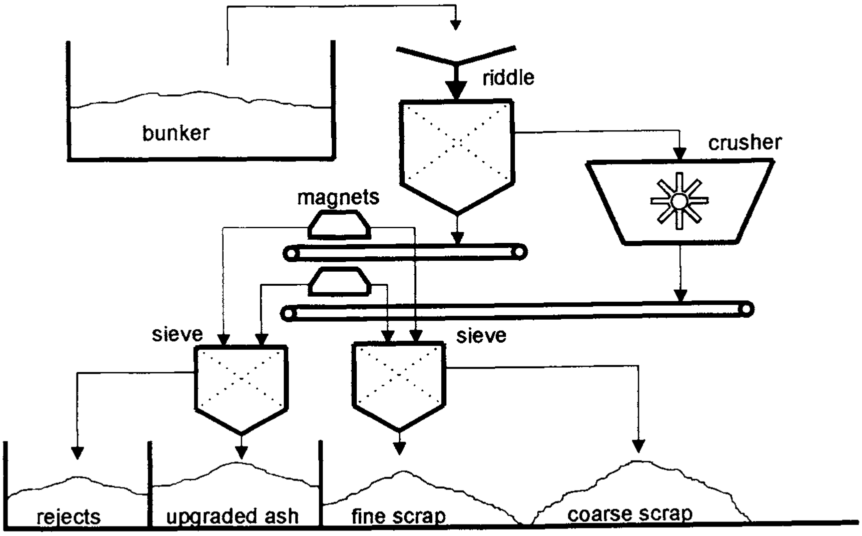
17.2.2 Metal Separation from Bottom Ashes

The quantity of ferrous and nonferrous metals in bottom ash is highly dependent on the effectiveness of the source separation programs in a given region, or on the presence of automated magnetic and eddy-current source separators used in the production of RDF. Bottom ashes from incinerator facilities can contain 7 - 10% ferrous scrap (Schoppmeier, 1988) and approximately 1 - 2% nonferrous metals. The economics of recovering these scrap materials is in turn dependent on the fluctuating market for scrap steel, and ultimately the demand for finished steel. Normally, primary scrap must be "de-tinned" and "decontaminated" of organic material in order to concentrate the iron inventory prior to use. This additional refining is reported to cost the equivalent of about $10 US per tonne of waste (Reimann, 1992). Ferrous metals processed through an incinerator are effectively "de-tinned" and relatively clean of organic contaminants, and thus are generally highly sought after as recyclable ferrous scrap.

In the case of bottom ash utilisation, the removal of ferrous and nonferrous metals must be completed prior to utilisation. Metals like Al, Fe, and Zn are susceptible to corrosion attack in an alkaline media resulting in the generation of hydrogen gas and corrosion products which may cause swelling, (especially metallic Al). Although it is common practise in most incinerator facilities to recover the ferrous scrap by means of magnetic separation, bottom ash utilisation requires its classification into specific grain sizes by screening, which is often combined with a magnetic scrap removal step (Göttlicher, 1990). This treatment is done either at the incinerator facility or at special treatment facilities. A schematic of a typical treatment technique is given in Figure 17.1.

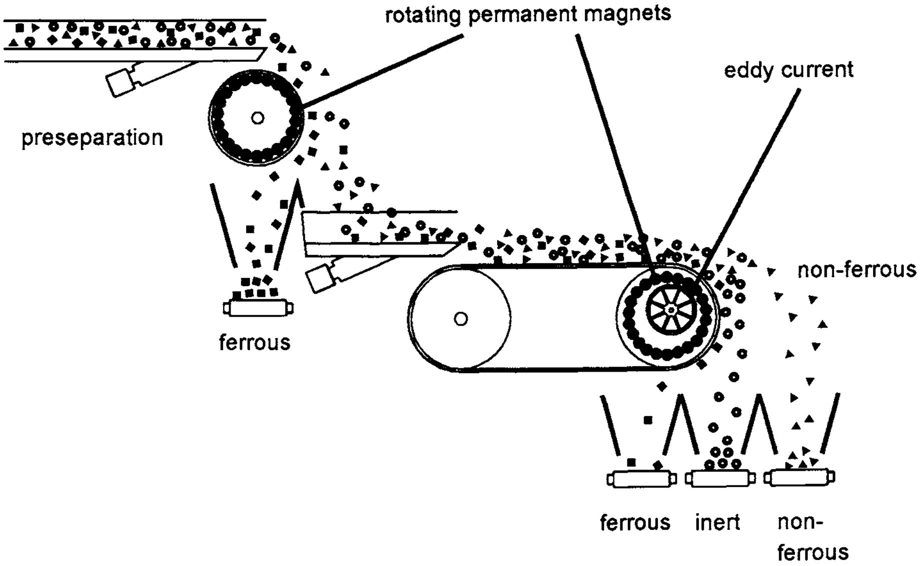
Generally, between 2 - 5 kg of nonferrous metals are present in a tonne of waste (see Chapter 2). In earlier times, some of these valuable materials were picked out of the ash stream by hand, however, a more efficient method of separating the material is the application of eddy current technology. The technology has not yet been widely applied, however, one example of a successful pilot-scale system was used to process the residues from a facility which employed a combination of pyrolysis, and high-temperature combustion of the pyrolysis gas and the carbon-rich fraction of the pyrolysis coke (at the 'Schwel-Brenn-Verfahren'). The eddy current system was used in combination with rotating permanent magnets to separate the ferrous metals, inert material, and nonferrous metals (like Al and Cu) (Berwein, 1990). A schematic of the applied separation technique is given in Figure 17.2.

Figure 17.1 Treatment of Bottom Ash by Screening and Magnetic Separation



Adapted from Göttlicher, 1990

Figure 17.2 Ferrous and Non-Ferrous Metal Separation by Magnets and Eddy Current



Berwein, 1990

17.3 PHYSICO-CHEMICAL AND CHEMICAL SEPARATION TECHNIQUES

Physico-chemical and chemical separation methods described in this chapter are characterised by more or less complex technologies which entail high operating costs. The following discussion presents these special processes following an ascending order of complexity of technology, which is typically directly related to the cost of the system. No distinction between pure physico-chemical, pure chemical, and combined methods will be made.

17.3.1 Washing Processes

Principles

The quality of incinerator residues, including their environmental compatibility (especially for bottom ash), is currently evaluated based mainly on the leaching behaviour of trace metals. A second group of contaminants, the soluble salts, especially chlorides, are now being recognised as potential problems by regulatory authorities as well. The simplest means of separating the soluble compounds from the solids is by washing.

Incinerator residues are generally highly alkaline. Contact with water typically generates a liquid with a pH ranging from 9.5 - 12. In this pH regime, most heavy and trace metals form hydroxides or other relatively insoluble compounds. Hence the efficiency of washing to facilitate metal extraction is very low, but a substantial removal of the soluble salts can be expected. If the pH exceeds values of 12, however, amphoteric metal compounds (such as some Pb and Zn compounds) are released and can remain in solution (van der Sloot et al., 1992; Environment Canada, 1993). Since the water consumption at most MSW incinerator facilities is severely limited, low L/S ratios are generally used to quench the ash. Consequently, there is a limited capability to remove the salts. This low L/S ratio, coupled with the short residence time of ash in the quench tank, typically prevents the process from reaching equilibrium. In recent years however, many investigations have tested the salt and metal removal efficiency of washing. Both options, the on-site washing (bottom ash only), as well as the secondary treatment in separate facilities have been tested from laboratory to full scale. Although there are benefits to these washing processes, they tend to generate a wastewater problem. If metals are dissolved, conventional wastewater technologies can be employed to reduce the concentrations of contaminants. However, the salts cannot be retained in wastewater treatment facilities. If their discharge is regulated, evaporation or complex membrane technologies must be applied. These technologies are expensive and, moreover, the question remains as to how and where the salt residues can be disposed.

Bottom Ashes

On-site Processes

The following represents some examples of different types of systems in use at various incinerator facilities.

Most incinerator facilities quench bottom ash in a quench tank filled with water. Previously, the only make-up water added was to replenish the losses due to evaporation and discharge of water along with the bottom ash. The quench tank, however, can also be used as a washing device if the water throughput is enhanced. As briefly mentioned above (see Section 2.2.1), the Zurich incinerator "KVA 1" tests on bottom ash washing were conducted using an L/S ratio of 10:1 (Buval, 1990). Only 0.1 - 0.2% of the heavy metals were solubilised and 82% of the chlorides were removed. However, reduction of the L/S ratio to simulate on-site washing reduced the yield of soluble chlorides. It was estimated up to 500 L per tonne of waste is required to guarantee acceptance under the Swiss TVA limit for utilisation in road construction, which translates into 1 gram of Cl per kilogram of ash (Bundesamt für Umweltschutz, 1988). The report also recommended the washing of fresh bottom ash was more effective than aged ash, since the chloride removal efficiency was significantly higher than from aged ash. Furthermore, the leaching of the ash with a CO_2 enriched water also needs to be considered. Under the CO_2 enriched conditions, some metals like Zn are easily mobilised, whereas other metals such as Pb and Cd form relatively insoluble carbonates and are not significantly affected by such treatment. It is speculated the overall intent of this application was to simulate the Swiss TVA leaching test, and thus allow facilities to meet the respective limits more easily. Whether this translates into an improvement of leaching stability in the natural environment has yet to be determined.

About 350 L of water per tonne of waste feed are used to wash bottom ash (L/S ratio of 1:1) at one German incinerator facility (Reimann, 1992). Published data indicate about 50% of the chloride can be removed from the bottom ash, which corroborates the Swiss test results mentioned above, whereas the removal of fluoride and heavy metals were not significant. Unfortunately, the data for alkali metals were not available.

Another process proposes to integrate treatment for all of the residues streams (the MR-Process), and involves washing of the bottom ash in a quench tank with an SO_2 scrubber solution (Stubenvoll, 1989). This process is discussed in more detail later (see Chapter 3.3.3.2). The washing is used as a separation step to remove the soluble salts from the ashes. The original intent of the process was to desaturate the SO_2 scrubber circulation fluid of sulphates by gypsum precipitation in the quench tank.

Secondary Processes

In some countries, the conventional conditioning required prior to bottom ash utilisation includes aging the ash, which involves storing the ash in piles exposed to the natural elements for at least a period of two weeks. This aging changes the chemical properties (see Chapter 9), but does not guarantee the ash will pass the regulatory leaching tests, even the German DEV S4 test. Therefore, consideration of washing the ash prior to use has been considered to enhance the aging process. Washing after, instead of prior to, aging was recommended in order to maintain the buffering capacity of the ashes, since alkalinity is regarded as an important parameter driving all of the aging processes. In full scale experiments, aged bottom ash was washed at an L/S ratio of about 1:1 (Lahl, 1992). Although the aged ash was already suitable for utilisation, the washing improved the DEV S4 results, especially with respect to the chlorides and alkali ions.

With respect to bottom ash weathering, a German study examined two different treatment options for bottom ash (Schneider 1994). Bottom ash from two facilities was stored outside in a pile (height 25 cm) for three months permitting an estimated 0.5 L/kg of precipitation to infiltrate the pile. Figure 17.3 illustrates the Cl release from this material was reduced by the same order of magnitude than it was by washing directly after discharge. Subsequent washing of the aged ash resulted in only a minor reduction in the Cl leaching, indicating little benefit was achieved by additional washing. In larger ash piles, the L/S ratio should be decreased substantially, and thus removal of Cl as well. Consequently, washing rather than aging, was recommended as the preferable method to stabilise bottom ash, since it was more effective at Cl removal and the Cl rich washing solutions could be treated within the incinerator facility (e.g. as feed solution for the wet scrubber).

Air Pollution Control Residues

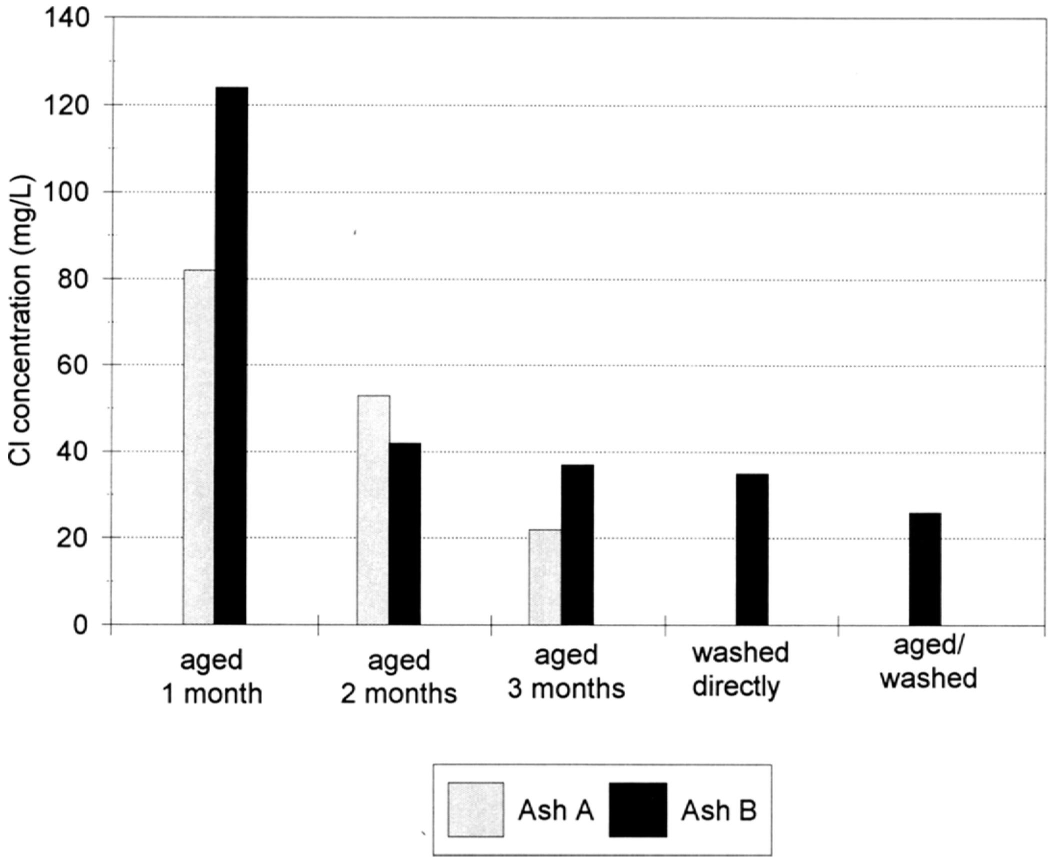
As mentioned previously, because APC residues and fly ash contain high concentrations of potentially mobile trace metals, soluble salts, and semi-volatile organic compounds, these residues are classified as "special" wastes in some countries. Since disposal strategies for hazardous wastes are generally expensive, and sometimes even limited within a specific region, efforts have been made to render the residues more suitable for conventional disposal strategies.

Swiss Fly Ash Treatment

From a geological perspective, Switzerland has only a limited capacity for hazardous waste disposal, and research into developing alternate means of disposing fly ash were initiated in the mid-1980's. Since most Swiss incinerator facilities employ wet scrubbing technology with wastewater treatment, the focus of much of the research has been on washing the residues prior to stabilisation with cement (Tobler, 1988). These stabilised residues must then meet the stringent limits for salt and trace metal release based on the Swiss TVA leaching test before being classified as suitable for landfill (Bundesamt für Umweltschutz, 1988).

Demonstration experiments were performed in a pilot-scale test facility where an L/S ratio of 2:1 was applied to remove the soluble salts (Dietler, 1990). The pH of most of the washed residues was about 10, resulting in a very minor release of trace metals into the wash water. However, some final pH values were mildly acidic (about pH 6). In these cases, the release of trace metals was sufficiently high to create problems in the wastewater treatment facility. In order to meet effluent discharge limits, especially for Cd and Hg, the organic additive TMT #15 was added to the solution to precipitate

Figure 17.3 Chloride Concentrations in the DEV S4 Test Solutions after Direct Washing and Washing After Aging of 3 Months



trace metals. (A more detailed discussion of this agent is found in Chapter 19.) The leaching stability of the washed fly ash alone has not been tested, but the solidified products pass the TVA test limits to permit disposal in a residue landfill. The process was deemed successful enough to be installed in a number of Swiss incinerator facilities.

Some changes with respect to cement quality and quantity are discussed elsewhere (Ponto, 1993). Unfortunately, the main disadvantage to the process is the salts, including chlorides and sulphates, which pass through the wastewater treatment facility and are subsequently discharged into the river systems. In addition, the long-term stability of the organic contaminants remaining in the products, and trace metal compounds formed with TMT #15 remains unknown. Should the organic components begin to degrade, it is possible the trace metals will become available for leaching.

17.3.2 Acid Leaching

The efficiency of washing processes to remove trace metals from MSW incinerator ash is limited, especially from fly ash and APC residues. Although trace metal concentrations in these residues are much higher than in bottom ash, the alkalinity of APC residues, especially from dry/semi-dry scrubber systems, is sufficiently high to promote the solubilisation of only amphoteric metals. Hence, extraction of other trace metals requires a significant addition of acid to reduce the pH to acidic levels. Some advanced processes, which are described in later chapters, combine separation with further treatment steps as an integrated approach to fly ash and APC residue treatment. However, the basis of extracting trace metals results in the release of salts, which creates a potential effluent discharge problem anywhere except marine environments.

Bottom Ash

An acid extraction process for trace metals from bottom ash was tested at laboratory scale in the Netherlands. The primary objective of the process was to improve the leaching stability of the ash (Buijtenhek, 1989). The tests compared simple washing of bottom ash with acid extraction. Screening tests were also conducted to determine the removal capability of chelate-forming agents as well.

Data from the multi-step extraction at a pH of 4 indicated promising results for some metals at high L/S ratios (i.e., >20:1), however, the overall extraction efficiency of the process was rather poor, since many metals in the bottom ash are solubility controlled. Therefore, the only tangible benefit achieved by the process is to treat the ash in the event it exceeds regulatory leaching criteria. Furthermore, the comparably high water consumption of the process may limit its applicability in many countries.

Filter and Boiler Ashes

3R Process

The 3R Process is a two-stage treatment process which combines an acid extraction of soluble trace metal compounds from boiler and filter ash with thermal treatment of the compacted extraction residues in the combustion chamber of an incinerator (Vogg, 1984). Application of the process is generally limited to facilities which employ wet scrubber systems. The flow diagram given in Figure 17.4 illustrates the use the acid flue gas cleaning solution as the extraction medium.

The process requires the separation of Hg from the scrubbing solution prior to the extraction of other trace metals. This separation is done by ion exchange and is discussed in detail later in the chapter. The L/S ratio is in the order of 7 - 10:1, and the final pH adjustment in the extraction vessel was 3 - 4. The residence time in the continuous flow system is about 30 minutes, achieving extraction efficiencies of approximately 90% for Cd, 70% for Zn, and 20 - 40% for other metals. Overall, about 20 % of the total solid matter is dissolved. The filtrate from the process must be treated prior to discharge, whereas the extracted residue is returned to the combustion chamber of the incinerator. If the economics are satisfactory, electrochemical or ion exchange processes can be used to separate out specific metals for reuse. When this is not cost effective, hydroxide precipitation is used to produce about 2 kg of concentrated inorganic residue per tonne of waste burned. The extracted residue is returned to the combustion chamber not only to destroy the PCDD/PCDF and other semi-volatile organic compounds present in the residue, but to further stabilise the heavy metals remaining in the residue through sintering (Vehlow, 1993).

The process has been successfully tested in pilot-scale for the extraction step, and has also been installed at full-scale at a Swiss incinerator facility. The recycling step has been successfully tested at full-scale (Vehlow, 1990). The preliminary results from the full-scale facility on the extraction step in Switzerland corroborate the findings of the pilot scale tests (Quittec, 1993). This process has been found to increase the cost of waste incineration by approximately $4 - 6 US/tonne of waste burned.

MR-Process

Another multistage process already mentioned in the discussion of on-site bottom ash treatment is the MR-Process (Stubenvoll, 1989). A flow diagram of the process integrated into an incinerator is given in Figure 17.5. The aim of this treatment process, like that of the 3R process, is to improve the residue quality by concentrating trace metals for potential recovery and reuse, and the destruction of organic contaminants.

The system operates by extracting the boiler and fly ash streams using the acid scrubbing solution from the first-stage wet scrubber. The washed and filtered residues are then heated in a rotary kiln for one hour at >600°C to destroy the PCDD/PCDF compounds and to volatilise the Hg. The off-gases are passed through an activated charcoal filter at 100°C where at least 95% of Hg is removed. The filtrate from the

Figure 17.4 Flow Diagram of the 3R Process

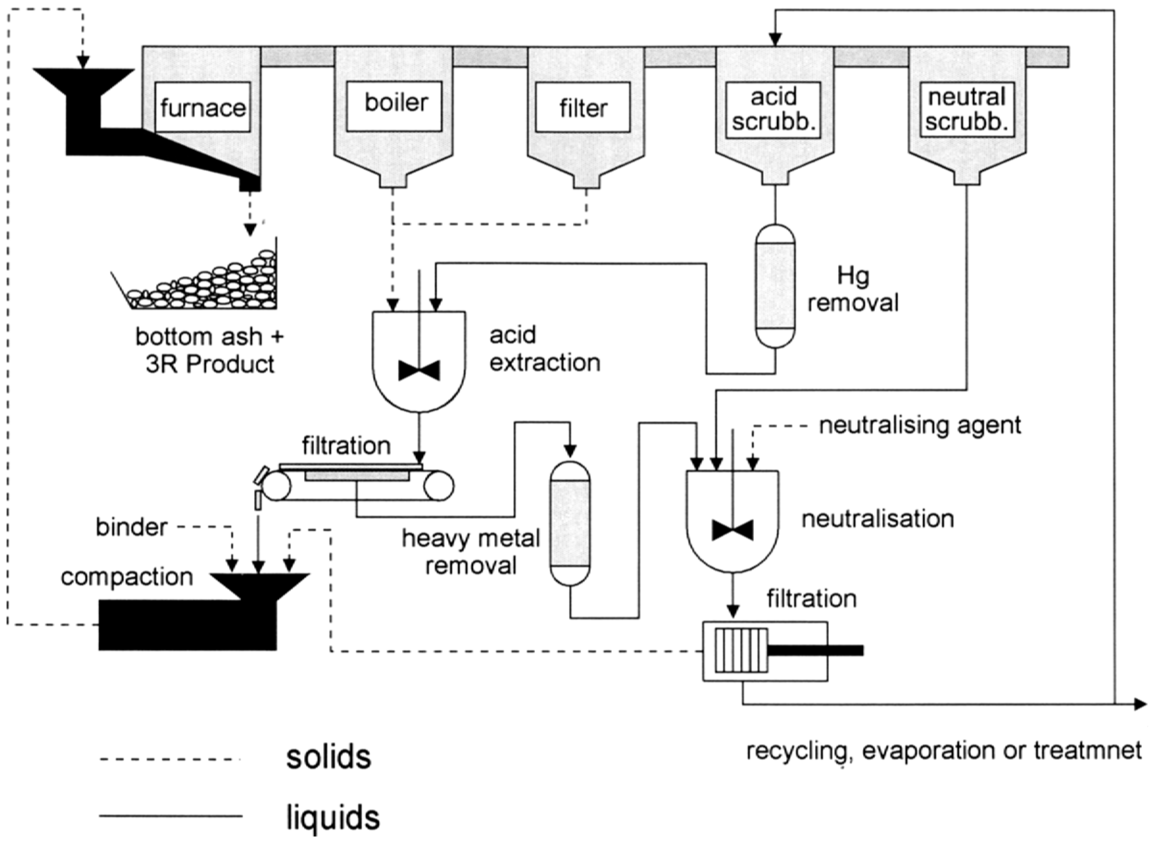
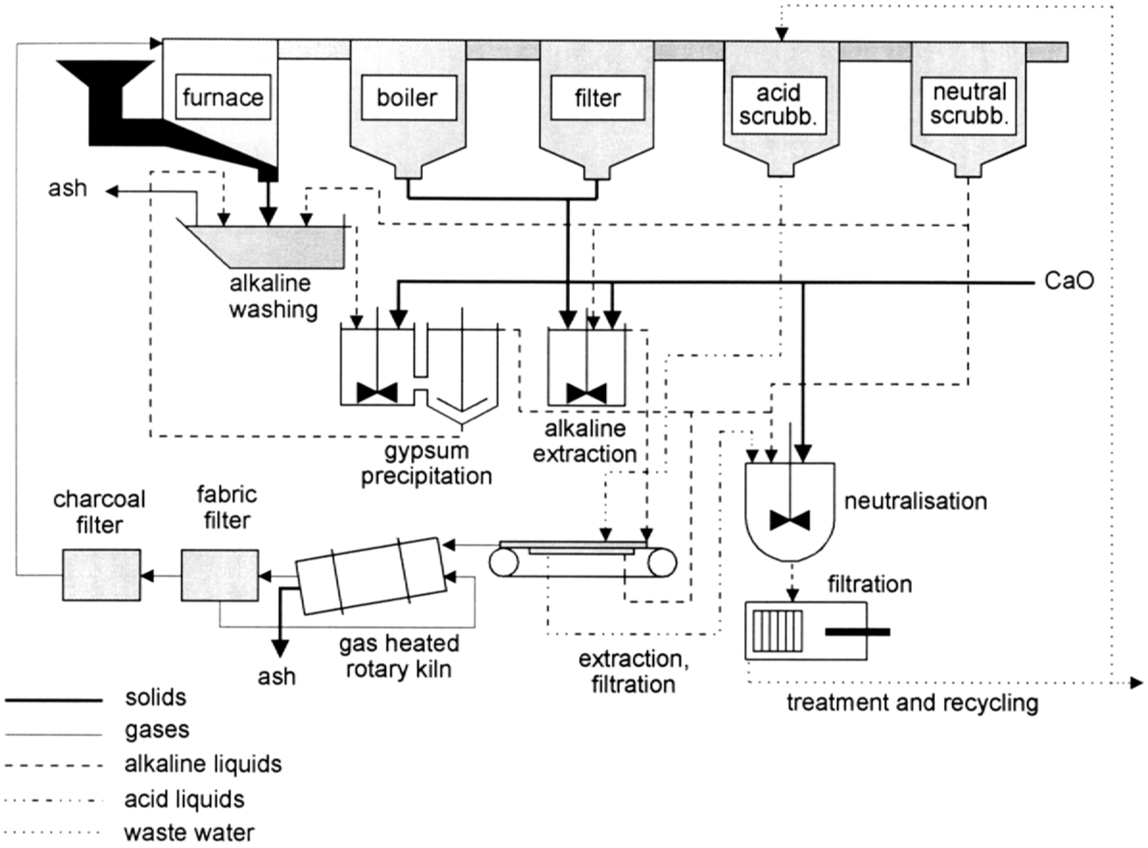


Figure 17.5 Flow Diagram of the MR-Process



Stubenvoll, 1989

extraction step is treated in a wastewater treatment facility. The effluents from the second-stage scrubber are used for on-site bottom ash washing, as well as for neutralising acidic effluent streams. The Hg laden charcoal must be treated or disposed of as a hazardous material since simply recycling the material back into the combustion chamber would only serve to release the Hg into the flue gas again.

FLUWA Process

The FLUWA process (Frey 1991), which is very similar to the extraction stage of the 3R process, has been tested in pilot and full-scale at two Swiss incinerator facilities. The acid flue gas cleaning solution is used (after Hg removal) to extract trace metals from the boiler and fly ash streams. At a typical Swiss gas cleaning L/S ratio of 4.5:1, an acid water stream with a final pH of 3 - 4 is generated. This solution is used to wash the residues which are then separated via vacuum belt filtration. Generally, the solid residues are capable of meeting the Swiss TVA leaching limits for residue landfills, while the extracted metals precipitated from the filtrate have the potential for recycling.

ALS Process

The ALS Process (Acid Leaching and Sulfide Process) is a metal extraction technology which is in commercial use in Japan. It consists of three stages:

- slurrying of fly ash and wastewater at an L/S ratio of 5:1
- adjusting the pH of the slurry to 6-8 with HCl to extract heavy metals. After the extraction, NaHS solution is added to change soluble heavy metals into stable compounds
- adding a coagulant to the extracted slurry and dehydrating the slurry using a hydroextractor

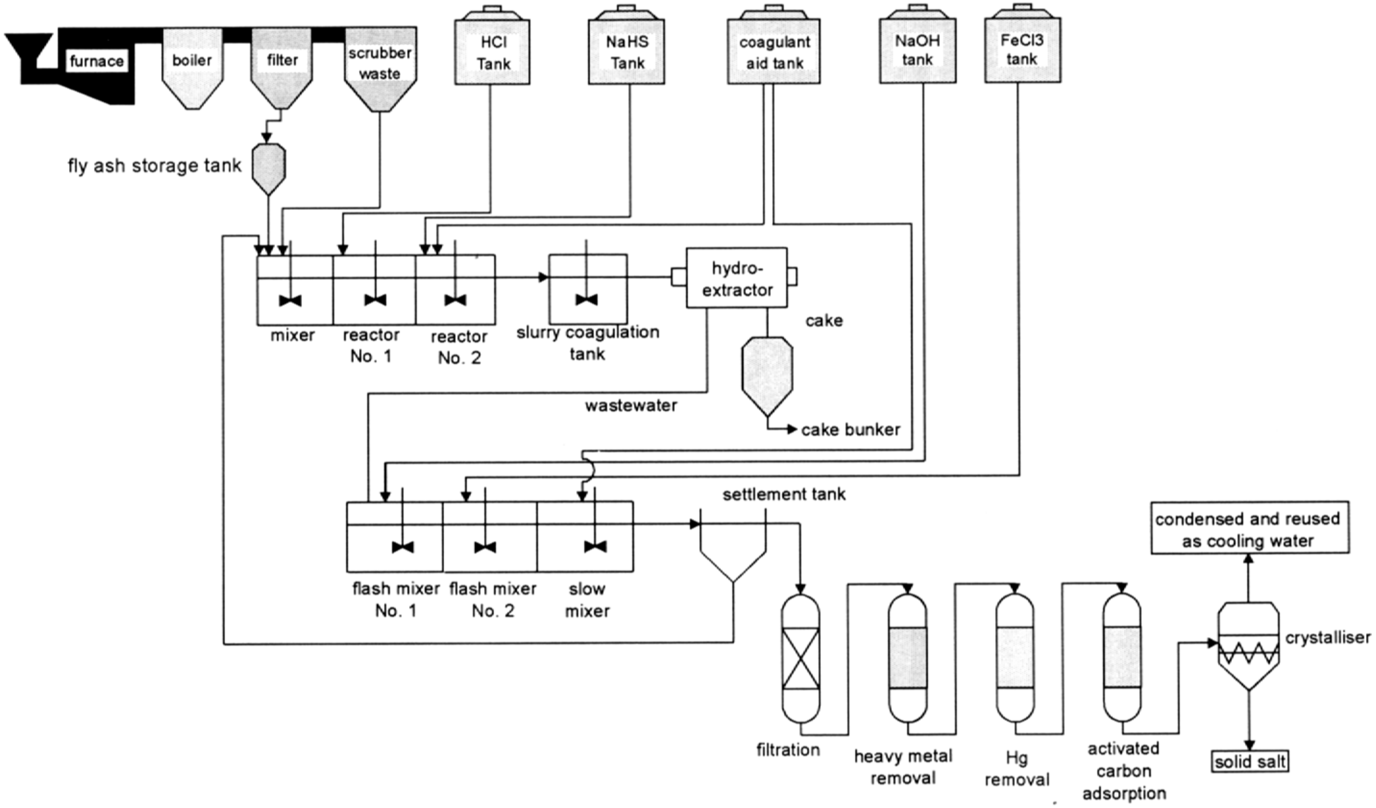
A process flow diagram of this system is provided in Figure 17.6.

17.3.3 Ion Exchange

Principles and Results

Ion exchange is a process widely used in chemistry, both for analytical purposes as well as for industrial chemical production. The process involves isolating or enriching single ions or groups of ions from multi-component solutions. Many specific exchange materials have been developed on the basis of zeolites, as well as organic resins. In most cases, ion exchange can be highly specific by using the proper exchanger and optimising the operation conditions. Ion exchange is often used in industrial wastewater treatment to remove metals. However, the application of conventional acid ion exchange resins to MSW incinerator wastewater streams are not effective due to the high Ca concentrations. Hence, resins which carry chelate forming organic groups like iminodiacetic acid (trade names are Amberlite IRC-718, Lewatit TP207 and TP208, Ionac SR-5) or bispicolylamine (trade name Dowex XFS4195) are the most preferred.

Figure 17.6 Flow Diagram of the ALS Process



Sakai, 1994

These resins have high removal efficiencies for specific metals like Co, Ni, Cu, Zn, Cd, and Pb (Jekel, 1992). In most cases, the ion exchange process is controlled by exchange equilibria which enables this method to be easily used to recover exchanged ions.

17.3.4 Hg Recovery from Flue Gas Scrubbing Solutions

Recently, a method has been described which uses a special ion exchange resin which consists of thiourea (trade name Lewatit TP214) to remove Hg from the acid scrubbing solution of a two-stage wet scrubbing system. This process is an integrated part of the 3R Process and has also been incorporated into the APC system of a sewage sludge incinerator (Braun, 1993). The removal efficiency of Hg using the resin is excellent and is independent of the Hg concentration in the feed. Feed concentrations in the scrubber water can range from 1 - 30 mg/L of Hg, and at a pH of <1 produce effluents with residual concentrations of approximately 20 µg/L. The maximum load is about 200 g of Hg on one litre of resin. The Hg can easily be recovered from the resin, and thus the process can be used to solve some of the Hg problems in incinerators equipped with wet APC systems.

17.3.5 Crystallisation/Evaporation

Principles and Results

The main constituents of wet flue gas scrubbing solutions are chlorides in the acid scrubber and sulphates in the neutral scrubbing stage. The related cation depends on the neutralisation strategy chosen at the facility, either Na or Ca based compounds. In some facilities, Na is used in the acid scrubber, whereas both Na and Ca are used in the neutral stage. In the latter case, gypsum can be produced as a substitute for natural gypsum.

The disposal options available for chlorides are generally limited since they are characteristically highly soluble in water. Disposal in open landfills is not recommended, and discharge into sewers or fresh water is typically prohibited. While relatively safe long-term disposal can be achieved by deposition in old salt mines, this is a rather expensive measure, and discharge to a marine environment is not always possible. Hence different techniques have been proposed to isolate and purify NaCl or $CaCl_2$ out of the salt mixture for reuse. In order to reuse the salts, trace metal contamination of the product must meet stringent standards. Although the isolation and purification techniques are not complex, they are generally multistage processes.

NaCl Production

NaCl production in order to recycle parts of the chlorine inventory of the waste back into chlorine-alkali electrolysis has been proposed (Exner, 1989; Dettmann, 1990; Thomé, 1992), however, these processes have also been criticised for not really closing the chlorine balance (Karger, 1990).

The process shown in Figure 17.7 is designed to treat the effluents from a conventional wet scrubbing system neutralised with lime. The first step involves converting the Ca salts into Na salts. The generated $CaCO_3$ is substituted back into the scrubbing system as a neutralising agent. Mg salts, as well as gypsum and trace metals, are removed prior to evaporation to produce a NaCl product. Since even the direct disposal of mixed salts requires neutralisation and solid separation, the economic benefits of this process are comparable to disposal of mixed salts. At one facility, the process is used to generate NaCl for on-site water conditioning (Dettmann, 1990). Other proposals have been made to recycle the NaCl, either as crystalline salt or as a concentrated brine, into the chlorine-alkali electrolysis to replace rock-salt. Both products can meet requirements limiting trace metal contamination.

In Japan, a few facilities recover NaCl from wastewater discharged from wet scrubber systems. After removing Na_2SO_4 and heavy metals by using $CaCl_2$ and Na_2S respectively, a NaCl slurry is crystallised by concentration through evaporation. The NaCl crystals are recovered from the solution by centrifugal separation generating a final product which is 99% pure and is sold to the chemical manufacturing industry as a raw material for NaOH production (Wada et al., 1981).

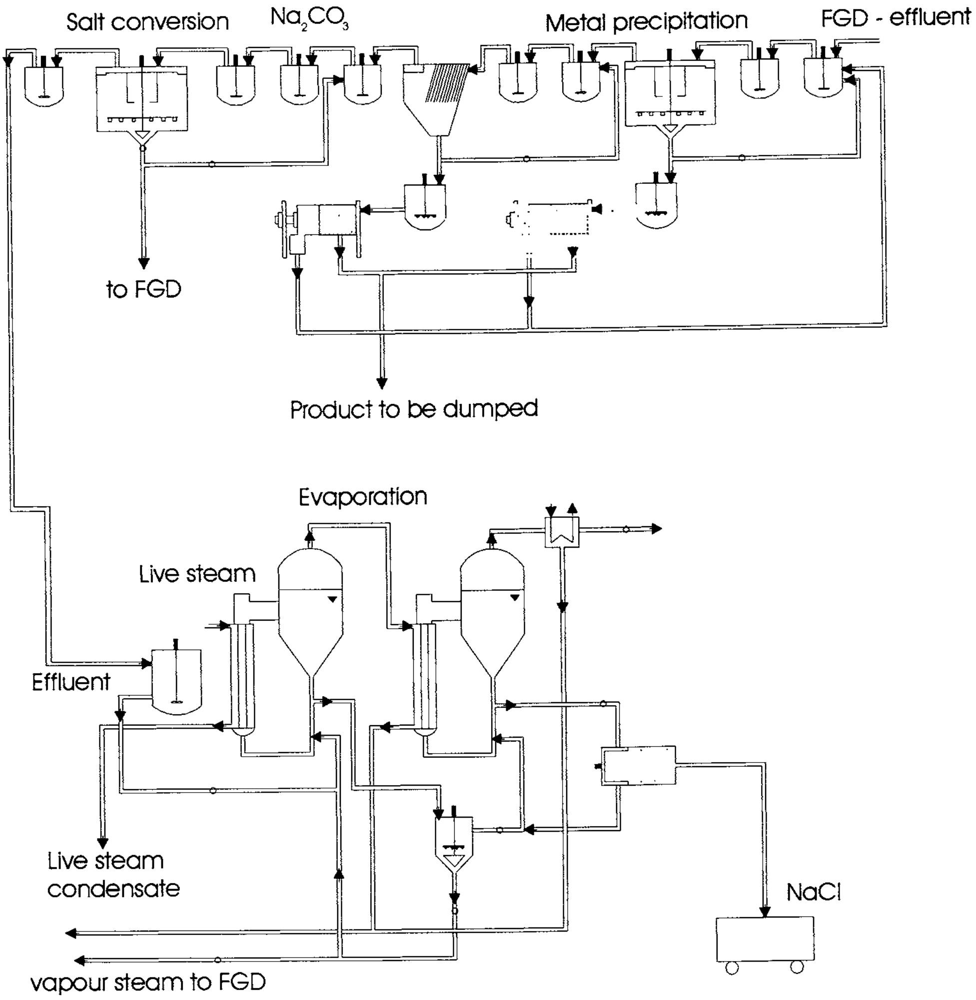
$CaCl_2$ Production from Dry/Semidry APC System Residues

Two different processes which combine washing and concentration of $CaCl_2$ have been proposed and tested in Canadian and Danish laboratory studies (Birch et al., 1993, Environment Canada, 1993). Although the results from the Canadian study were not available, the results from the Danish study indicate it is technically feasible to recover marketable $CaCl_2$ from dry/semidry gas cleaning residues by countercurrent washing (using water). A schematic for the process is shown in Figure 17.8. However, if the scrubber residues contain fly ash, some of the trace metals may be dissolved, which need to be removed by the addition of hydroxide and TMT #15. The filtrate is then subjected to evaporation and precipitation to partly remove Na and K. The $CaCl2 \bullet 2H_2O$ contains 3-7% by weight of alkali ions and can be commercialised. The filter-cake is then stabilised using cement, however, the effect of the hydroxide and TMT #15 on the sludge is not known.

Gypsum Production

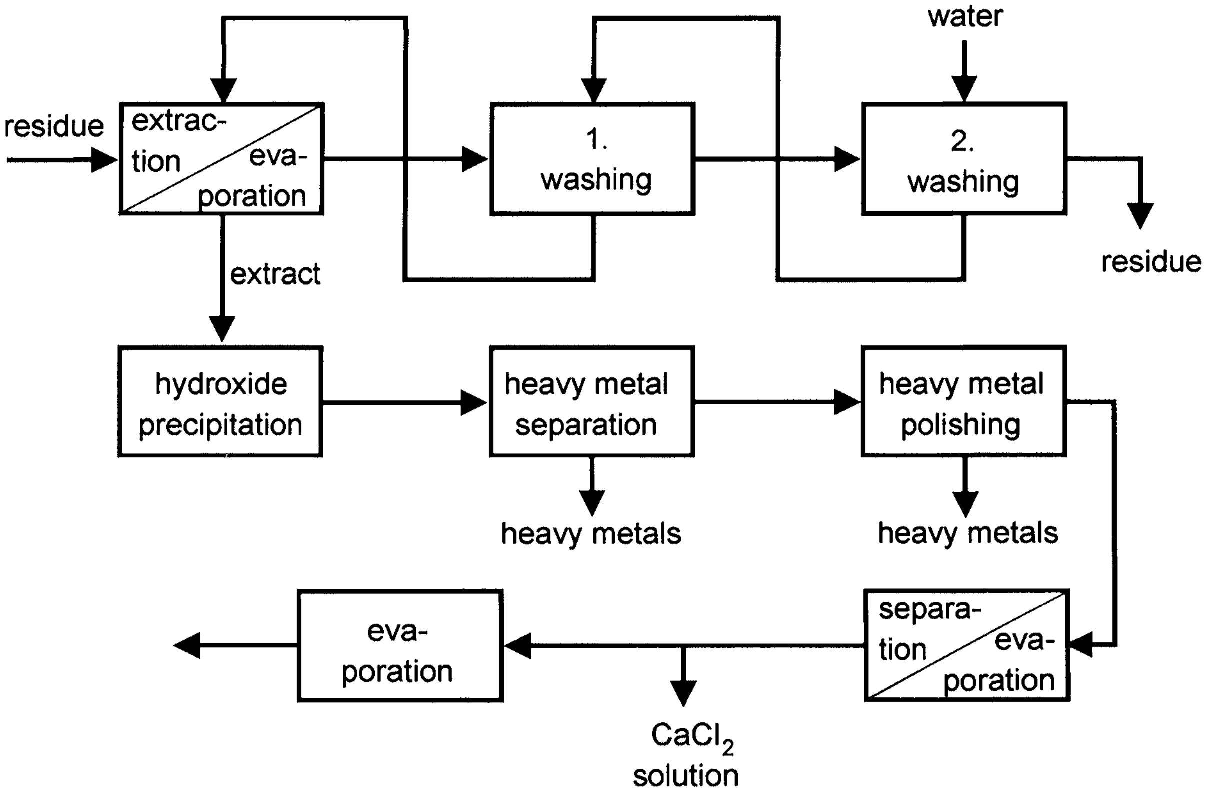
The production of gypsum from the effluents of SO_2 scrubbers is a widely used technology. The first experience with the process was acquired with the desulphurisation of coal-fired power station residues back in the early 1980's, and the systems are the same as those used for residues from coal-powered stations. The purification of gypsum in order to meet standards set for its utilisation is a proven technology.

Figure 17.7 Flow Diagram of NaCl Recycling



Exner, 1989

Figure 17.8 CaCl2 Production from Dry and Semi-Dry Flue Gas Cleaning Residues



Adapted from Birch, 1993

17.3.6 HCl Recovery by Distillation

Principles and Results

HCl present in the flue gases is trapped in the acid gas removal stage of a wet scrubbing system, forming dilute HCl. This acid is very volatile and distillation processes are an obvious option for HCl recovery. Under normal pressure, HCl forms an azeotropic mixture with water at a concentration of 20% HCl. To achieve higher concentrations additional treatment is required. Some of the typical difficulties encountered during distillation of HCl in flue gas scrubbing solutions are due to the HF, HBr, SO_3, dust (trace metals), and organic compounds which are also present in the flue gas. Consequently, the primary HCl in the HCl absorber contains many unwanted contaminants.

Different strategies have been developed to distil HCl from flue gas scrubbing solutions. Depending on the desired concentration of the product and on the operation conditions of the first scrubber, there are minor variations in technology.

Proposed Processes

A relatively simple process applied in a two-stage wet scrubbing process produces marketable HCl in a secondary facility. A flow diagram of the system is given in Figure 17.9 (Juritsch, 1989). The process includes combined gypsum and Na_2SO_4 production from the effluents of the neutral scrubber. A potential problem with fluoride contamination of the HCl is addressed in a similar process combining distillation of HCl from the acid scrubbing solution and the production of gypsum from the neutral scrubber (Kürzinger, 1989).

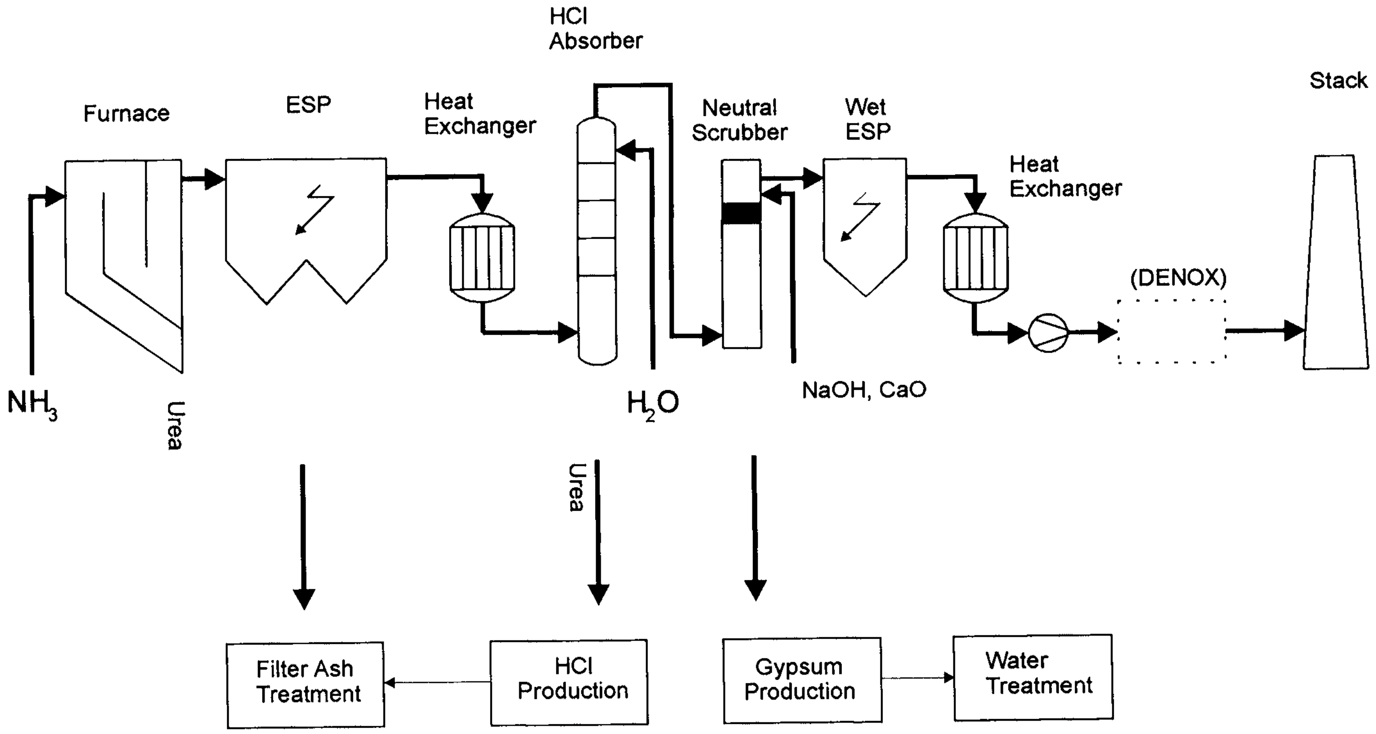
In modern wet scrubber systems, pre-neutralisation of the acid scrubbing solutions is common practice to conserve water. This neutralisation is preferentially done using lime, which is relatively inexpensive. If HCl is to be distilled from pre-neutralised scrubber water, an intermediate step of salt conversion is required. A process dealing with this option is given in Figure 17.10 (Karger, 1990).

17.3.7 Electrochemical Processes

Principles and Results

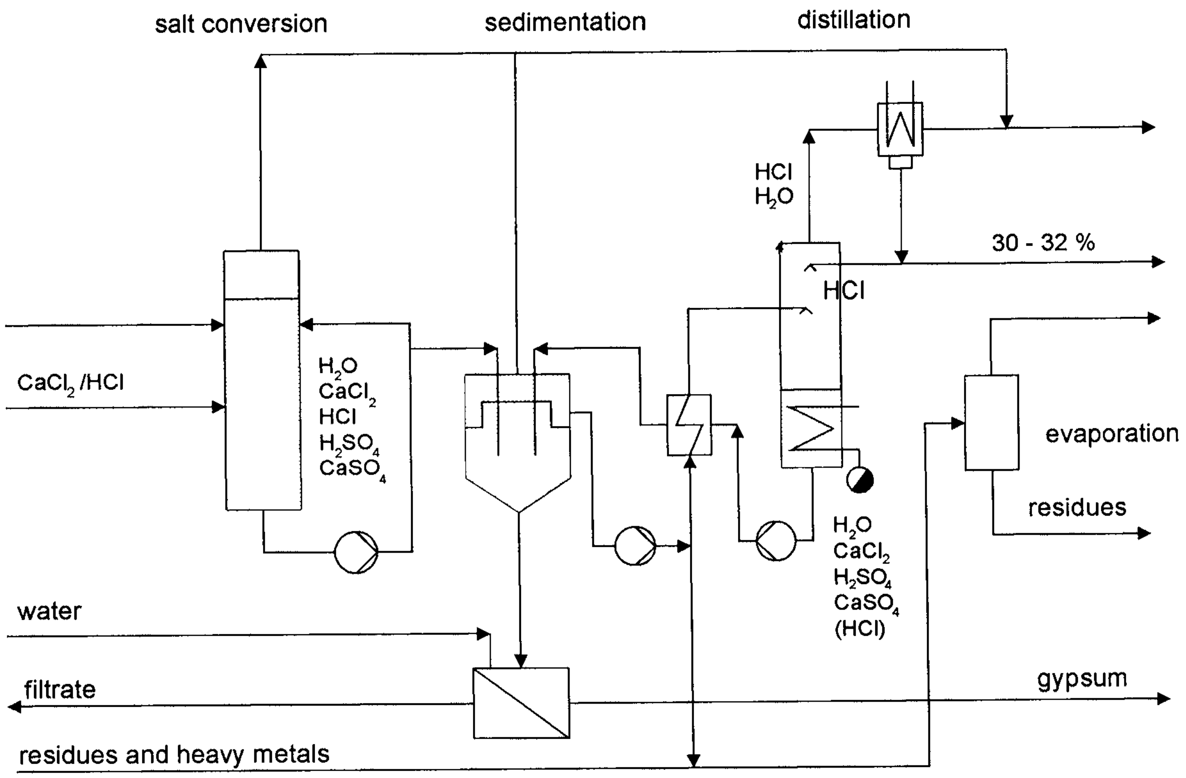
Electrochemistry is a conventional technology widely used in industry to refine noble metals, produce chlorine at the industrial scale (chlorine-alkali-electrolysis), and to generate hydrogen from water. The main advantage to electrochemical processes versus chemical-based processes is that they require no additional chemicals, and thus create no new residue problems. According to the different electrochemical potentials of the specific chemical compounds, processes can be tailored to isolate and concentrate specific components out of even very dilute solutions. However, these advantages are accompanied by some disadvantages which include high operating and capital costs and the need for highly trained, experienced staff.

Figure 17.9 Flow Diagram of HCl Recovery



Juritsch, 1989

Figure 17.10 Flow Diagram of Hcl Recovery from Ca Containing Solutions



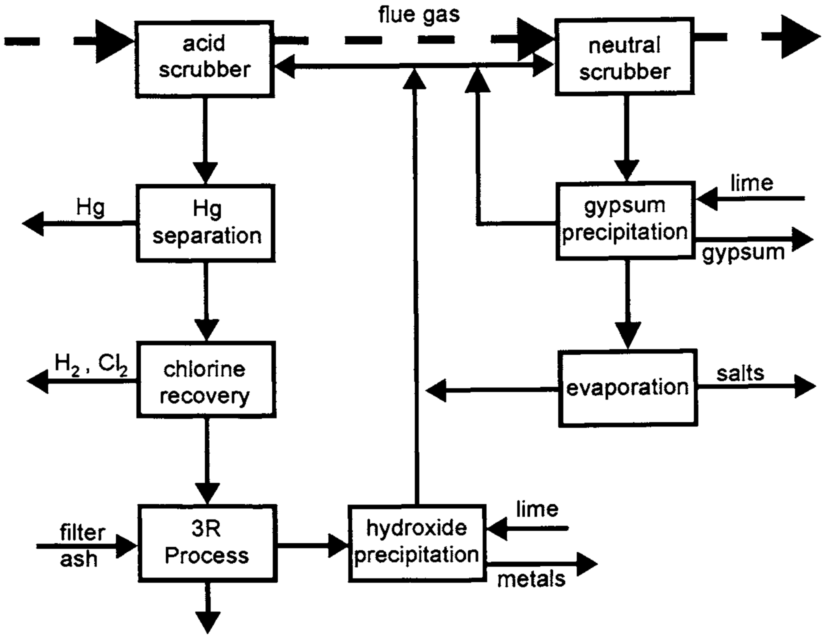
Karger, 1990

An example of an electrochemical process is based on the experience gleaned from the galvanising industry which could be used to develop an electrochemical Hg recovery system from flue gas scrubbing solutions. Theoretically this very specific process could generate a high yield, however, no full scale applications have been established.

Chlorine Recovery

On the basis of laboratory experiments, a proposal has been made to separate chlorine by direct electrolysis of the acid scrubbing solution (Volkman, 1991). In a bench-scale demonstration, current efficiencies of up to 60% could be reached. It is anticipated that a full-scale installation would consume about 3% of the energy produced by an incinerator to recover about 70% of the Cl inventory of the waste. However, about 6 kg of soluble salts per tonne of waste remain in the solutions. Since these salts are not desirable, they must be disposed. Hence the process will not close the Cl circuit completely, but it contributes to reducing the loading to local disposal sites. This proposed process has been designed as an integral part of the 3R Process for metal extraction out of filter ashes, and with gypsum production from the sulphate present in the second scrubber. A flow diagram of this combined process is given in Figure 17.11.

Figure 17.11 Flow Diagram of a Combination of the 3R Process and Electrochemical Chlorine Recovery



Volkman, 1991

Common to all of the recovery technologies, is the need to evaluate the economic benefit/disadvantages based on the supply and demand for the recovered material within regional markets. For example, the gypsum market in most countries is generally not conducive to recovery from MSW incinerator residues due to the natural abundance of the material, and the availability from secondary sources, such as from coal-fired generating stations. In addition, the stigma associated with products derived from MSW incineration, may limit the potential use of the recovered material. In all cases, the recovery of a material from a residue stream should be compared against the expense of a direct disposal in an adequate disposal site. Given the costs of proper disposal and the problems associated with siting disposal facilities, recovery of materials from incinerators may yet prove to be economically viable.

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