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MSWC salt residues: Survey of technologies for treatment

TNO Environment, Energy
and Process Innovation

TNO-MEP
Business Park E.T.V.
Laan van Westenenk 501
P.O. Box 342
7300 AH Apeldoorn
The Netherlands

Phone: +31 55 549 34 93
Fax: +31 55 541 98 37
Internet: www.mep.tno.nl

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Author(s)

L.P.M. Rijpkema

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ECVM

Attn. Mr. J.P. De Grève

Av. E. van Nieuwenhuysse 4, Box 4

B-1160 BRUSSELS

Belgium

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Summary

In municipal solid waste combustion (MSWC) facilities, flue gas cleaning results (among others) in solid residues, mainly from the adsorption and neutralisation of acidic gases like HCl and SO₂. Due to differences in flue gas cleaning system set-up the amount and composition of these residues vary enormously between facilities, but in most MSWC facilities these residues represent a considerably large waste stream, which has to be landfilled as hazardous waste.

In the underlying study the possible technologies to reduce the amount of these residues ending up in these (expensive) hazardous waste landfill sites are briefly reviewed.

As mentioned, neutralisation residues largely differ, dependent on the type of flue gas cleaning applied, both in amount and composition. As a consequence the technologies often apply to a specific type of residue generated by one of the possible flue gas cleaning systems and is not applicable to all neutralisation residues.

It appears that the majority of the technologies focuses on the neutralisation residues from the absorption of HCl by wet scrubbers, which evaporate the cleaned wastewater. In this type of plants the absorption of SO₂ (in the second step of the wet scrubber) leads to filtercakes in which gypsum is a major component. Due to its low solubility in water and to very poor market potential, these SO₂-related neutralisation residues are not (yet) interesting for upgrading or recycling efforts.

The HCl related residues, however, can be either upgraded to a commercial grade concentrated hydrochloric acid or be upgraded to calcium chloride (solution). For this concentrated hydrochloric acid limited market potential exists and the feasibility depends on the possibilities for setting up long-term contracts.

The calcium chloride (solution) suffers a poor market potential and from an economical point of view can best be discharged (after purification) into (saline) surface water. The nearby presence of such water and the permit to discharge of the calcium chloride then become decisive parameters.

By recycling the HCl-related residues and not touching the SO₂-related residues, the total amount of solid residue to be landfilled is reduced by approximately 50%.

For neutralisation residues from dry and semi-dry scrubbers not many possibilities for upgrading or recycling exist. Mainly this is due to the complexity of these residues. A good solution for these residues is offered by the Neutrec process, which uses sodium bicarbonate as reagent in the scrubbers and which can recycle, after treatment, the produced residue in a soda plant.

An overview of the 5 most promising technologies, which were looked into in more detail, is given in Table 1.

Table 1 Characteristics of technologies for reduction of the amount of neutralisation residues to be landfilled.

Technology	Commercial products	Status of development	Solid residue to be landfilled [kg/tonne MSW combusted]	% reduction of residue to be landfilled ^{1,2}	Economical feasibility	Technical feasibility	Comments ²
Production of hydrochloric acid (chapter 3.1)	Concentrated hydrochloric acid (15 – 30 wt%)	5 plants in operation, 3 under construction (all in Germany)	10	33% (B) -294% (A)	Yes, proven	Yes, proven	Applicable to wet scrubber systems only; sensible for B. Market potential for HCl acid limited. Filtercake (SO ₂ related) not touched.
Neutrec process (chapter 3.2)	Feedstock for soda plant	- Scrubbers (approx. 20) in operation since 1991 - Recycling of residue: 1 industrial pilot plant in operation; more capacity planned	³ 1.2 (dry matter)	³ 94% (C) 95% (D)	Yes, indicated	Yes, proven	Applicable as a retrofit to C and D. Recycling capacity yet to be extended, but not seen as a limiting factor.
Recycling of salt residue (chapter 3.4)	Calcium chloride	Pilot plant experiments executed	7.4 to 10.4	31 to 51% (B)	Yes, possibly	Yes, probably	No market for calcium chloride expected: discharge in surface water? Applicable to B. Filtercake (SO ₂ related) not touched.
Recycling of salt residue: special case (chapter 3.4.1)	Calcium chloride	Industrial pilot plant just started operation	7.0	~ 50% (B) ~ 65% (C) ~ 72% (D)	Yes, in this special case	To be demonstrated by pilot plant	Special case: revenue from CaCl ₂ not necessary: discharge in surface water? Applicable to B. Maybe also applicable to C and D. Filtercake (SO ₂ related) not touched.
Adjustment of flue gas cleaning system (chapter 3.5)	Calcium chloride	Concept, composed of existing technology	7.2 to 7.4	51 to 52% (B)	Yes, probably	Yes, probably	Applicable to B only. Market for CaCl ₂ not needed: discharge in surface water? Filtercake (SO ₂ related) not touched.

¹ The percentage reduction is indicative and is specified relative to flue gas cleaning configurations as given in Figure 1 with the amounts of solid residues produced as specified in Table 1. A negative value indicates an increase of the amount to be landfilled.

² The configurations are indicated by letters: A = wet scrubber with effluent discharge, B = wet scrubber with effluent evaporation, C = semi-dry scrubber and D = dry scrubber.

³ The amount given includes the recycling of the flue gas cleaning residue. Without that (just application of a dry scrubber operated with sodium bicarbonate) the amount of residue to be landfilled is 15.7 kg per tonne MSW combusted and the percentages in reduction of landfill volume drop to 23% (C) and 38% (D).

Other promising technologies for dry scrubber residues are the TREFID process and the process offered by Taiheiyo. Both will however have to be demonstrated yet and success will largely depend on the acceptance of the products by cement plants.

Next to technologies, which reduce the amount of neutralisation residues, technologies exist to upgrade the quality of the residues to enable easier (cheaper) landfill. For improvement of the quality of the residue (decreasing the leachability) most often immobilisation techniques are applied, most commonly with cement or cement-like waste materials or by-products.

Vitrification and washing processes are technically feasible for fly-ash, but for neutralisation residues they are hardly ever applied (yet).

The economical feasibility of a certain technology is very plant-specific as many differences in circumstances (prices, regulations, politics, etceteras) between facilities are of influence. Therefore, the economical feasibility has to be redetermined individually, per plant.

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Appendix A

1. Introduction

MSWC (municipal solid waste combustion) facilities generate energy while reducing the volume of municipal solid waste and converting it into inert matter. In modern MSWC facilities, the necessary flue gas cleaning (FGC) system results in solid residues, which, depending on the FGC configuration, contain salts from neutralisation of acid gases (HCl, HF, SO₂). Until now, these residues are landfilled in a controlled manner (usually as hazardous wastes), which means a contribution to the processing costs¹ of MSW.

In previous studies it was revealed that the share of PVC waste products (present in municipal solid waste) in these residues can be significant (typically between 2 and 35%, depending on flue gas cleaning configuration), due to the fact that in MSW PVC is one of the major sources of chlorine, accounting for 30 to 70% of the chlorine input of the MSW combustion facility.

Based on these findings, ECVI asked TNO to draw up a survey of technologies, which may either reduce the amount of salty MSWC residues produced or improve the quality of these residues, so that these may be more easily discharged of, i.e. at lower cost and/or lower environmental impact. Furthermore, the potential of these technologies to contribute to the reduction of the salt residue discharge issue should be assessed.

However, since resources for this study are limited, the scope of this study is to give a first impression.

The study focuses on the following processes, because at the beginning of the study these were seen as potentially interesting for reducing the amount of solid residues from flue gas cleaning to be landfilled:

- flue gas cleaning configurations at MSWC facilities, which produce hydrochloric acid instead of salt residues;
- the Neutrec process, which uses an alternative reagent for acid gas neutralisation;
- a Danish process, which produces calciumchloride as salt for icy roads (road salt);
- recycling of the salt residues or reducing the volume of salt residues generated as investigated in the Netherlands.

Before these techniques are discussed, a brief outline of the normal current practice at MSWC facilities is given.

¹ The 'processing costs' are the actual costs incurred by a MSWC plant operator. 'Net processing costs' are the net result of capital cost, variable cost and energy revenue (from electricity sale). The 'gate fee' is the amount charged for acceptance of MSW and thus is equal to the 'processing costs' plus a commercial cost price element, which can be either positive (gate fee > processing cost: plant makes a 'profit') or it can be negative (gate fee < processing cost: plant accepts a 'loss').

2. Salt residue production at a MSWC plant

For the description of the way salt residues are normally produced at MSWC plants, here a short description is given, taken from [Rijpkema, 1999], where this is described in more detail.

Upon the combustion of municipal solid waste, flue gas is generated, which contains, among others, acidic gases of which HCl and SO₂ are the ones to be considered when looking at salt residue production. This flue gas is cleaned in a flue gas cleaning section, which covers the removal from the flue gas of fly-ash (dust), acidic gases (mainly HCl, SO₂ and NO_x), heavy metals and dioxins. The removal of the acidic gases HCl and SO₂ can be achieved by using different kinds of gas scrubbers: dry scrubbers, semi-dry scrubbers and wet scrubbers¹. Though many configurations are possible, this study recognizes 4 commonly encountered configurations, which are capable of meeting the strictest emission guidelines (like in the Netherlands and Germany) presently imposed upon MSWC for HCl and SO₂. The following configurations are involved:

- A. wet scrubber system with scrubber effluent discharge²
- B. wet scrubber system with scrubber effluent evaporation²
- C. semi-dry scrubber system
- D. dry scrubber system

These configurations are schematically drawn in Figure 1 and a short characteristic on each of these configurations is given in Table 2. Naturally, the figures given are typical values as individual differences between facilities will occur.

¹ In literature, different names are used for characterising scrubber types. 'Semi-dry' is sometimes used to refer to a dry scrubber which has water injection prior to the addition of the dry sorbent. Other refer to such a configuration as a 'conditioned dry scrubber'. Here a dry scrubber is assumed to have water injection prior to sorbent injection, as dry scrubbing without previous water injection is not considered to be state-of-the-art. In this study, 'semi-dry' indicates that the added sorbent is not a dry powder but a slurry in water. In other studies the latter configuration is sometimes referred to as 'semi-wet'.

² In Europe, actually, two types of wet scrubbers with effluent discharge are operated. The first type is represented by configuration A, where 2 effluents are discharged, one with dissolved Cl-salts and one with dissolved S-salts (sodium sulphate). The other type discharges of the Cl-salts through a cleaned liquid effluent, but the S-salts are precipitated as gypsum and end up in the filtercake. This second type can be derived from configuration B by disregarding the spray dryer. The filtercake produced can be considered identical (in composition and amount) to the filtercake produced by configuration B.

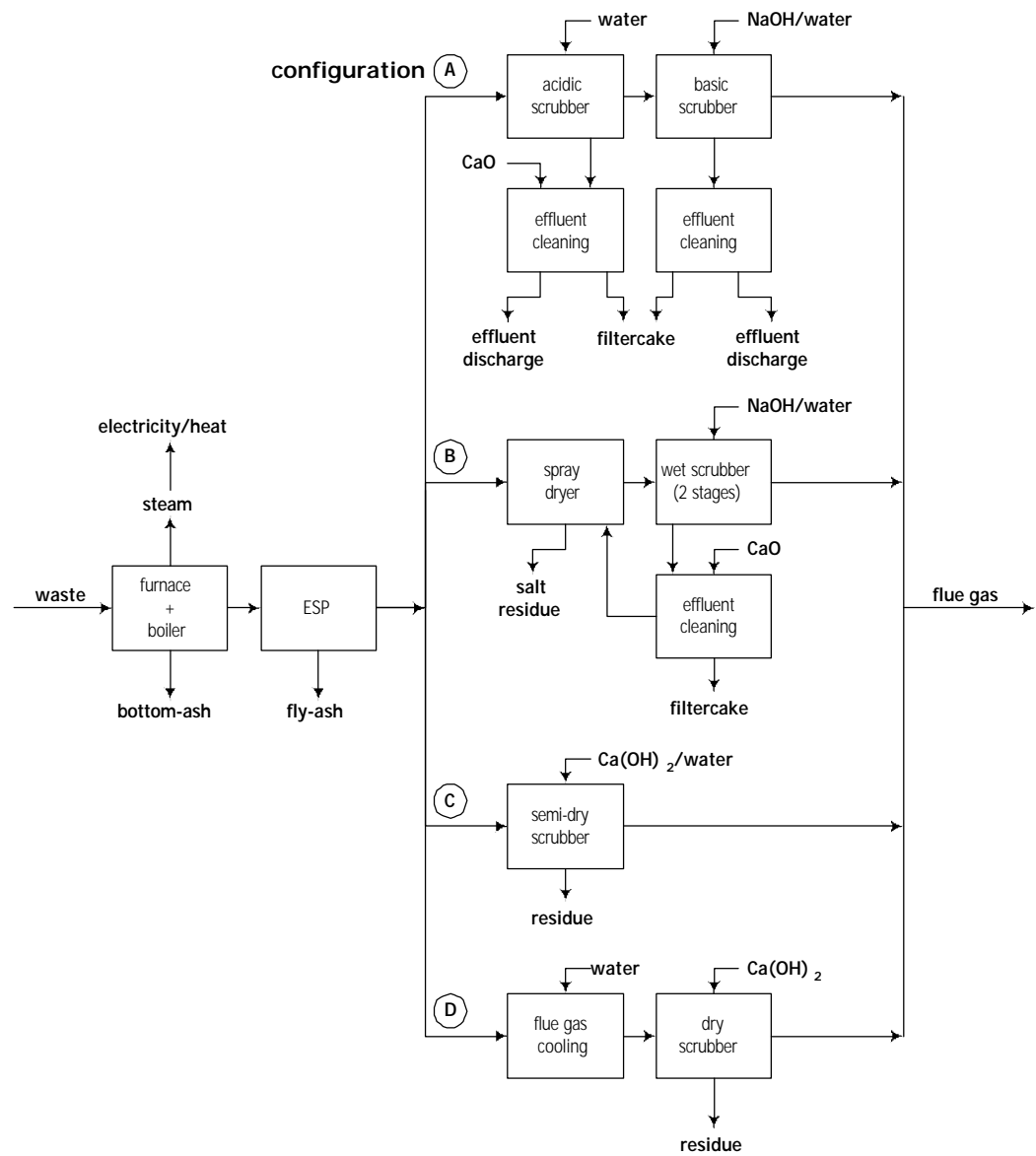


Figure 1 Examples of four often encountered flue gas cleaning configurations. (The spray dryer, semi-dry and dry scrubber consist of a reactor plus a subsequent filter. For clarity, the filters have not been drawn separately).

Table 2 Flue gas cleaning configurations with brief characteristics.

FGC Configuration	Reagents	Stoichiometry ¹	Residues	Amount of residue ² [kg/tonne MSW]	Main components
Configuration A: Wet scrubber with effluent discharge	NaOH (for SO ₂)	1.05 (1.0-1.5)	Filtercake	1.6	fly-ash, excess lime
	CaO (for neutralisation HCl)	1.1 (1.0-1.3)	2 Liquid effluents	not applicable	CaCl ₂ (in water) Na ₂ SO ₄ (in water)
Configuration B: Wet scrubber with effluent evaporation	NaOH (for SO ₂)	1.05 (1.0-1.5)	Filtercake	6.9	gypsum, fly-ash, excess lime
	CaO (for neutralisation HCl)	1.1 (1.0-1.3)	Salt residue	8.1 ³	CaCl ₂ , NaCl, fly-ash
Configuration C: Semi-dry scrubber	Ca(OH) ₂	1.8 (1.5-3.0)	Mixed solid residue	20.3 ³	gypsum, CaCl ₂ , fly- ash, excess lime
Configuration D: Dry scrubber	Ca(OH) ₂	2.5 (2.0-4.0)	Mixed solid residue	25.4 ³	gypsum, CaCl ₂ , fly- ash, excess lime

¹ Stoichiometry based on amount of acid gases in the flue gas: mole equivalent reagent / mole equivalent sum (HCl + SO₂ + HF). The first value given is the typical value used: between brackets a range of encountered values is given.

² Typical values of solid residues from the combustion of 1 tonne MSW are given. Amounts are given on a dry basis.

³ Here it is assumed that CaCl₂ in the residue does not contain crystal water.

Assuming, like in [Jacquinot, 2000], that each mole of CaCl₂ includes 2 moles of crystal water leads to increased amounts of salt or mixed solid residues:

- for config. B: 8.9 kg/tonne MSW (instead of 8.1)
- for config. C: 22.5 kg/tonne MSW (instead of 20.3)
- for config. D: 27.6 kg/tonne MSW (instead of 25.4).

The figures given in Table 2 were calculated for a typical MSW and PVC composition, the same as used in [Rijkema, 1999]. In Appendix A the data used are summarised.

3. Description of the technologies

In this chapter first encountered technologies to decrease the amount of solid residues to be landfilled are discussed (chapters 3.1 to 3.5). A description of the technology is given and the feasibility is discussed. Then (chapter 3.6) some technologies are mentioned, which (in general) do not decrease the amount of residue to be landfilled, but improve the quality of the residues, thus facilitating landfill, i.e. enabling landfill at cheaper landfill sites (with less pollution prevention measures). Finally, in chapter 3.7, other technologies are mentioned, which, at present, may offer less potential for a significant contribution in the solid neutralisation residue issue, but still are worth mentioning.

3.1 Production of hydrochloric acid at MSWC facilities

In Germany, a growing number of plants (5 at the moment, 3 under construction [*Jacquinot, 2000*]) has a different way of operating the wet scrubber. The purpose of these plants is to absorb the HCl from the flue gases separately and to upgrade this solution to a commercial grade. In order to achieve a concentrated solution the first step of the wet scrubber usually consists of at least two absorption steps over which the effluent is recirculated. The resulting HCl solution contains 10 to 12% HCl. As the azeotropic concentration of HCl in water lies around 20% it should be decided to what level the concentration has to be raised: above or below this azeotropic concentration. The production of an HCl solution just below 20% is much easier (less effort in upgrading processes, less additive consumption and less solid residues) but also has much less market potential [*Cousin, 1993*]. Upgrading the concentration to around 30% therefore is commercially more attractive.

This upgrading is achieved by applying a series of processes [*Menke, 1999*]:

- removal of HBr and HI by stripping the solution with NaOCl; Br₂ and I₂ evade as gases, which are absorbed in a NaOH-scrubber;
- removal of HF by adding AlCl₃ to form AlF₃ and (3) HCl;
- distillation and concentration to a 17% HCl solution;
- desorption of HCl by adding CaCl₂ to the solution: HCl evades as a gas and is absorbed in demineralised water to form a 30% HCl solution, which can be sold commercially.

Typical values: a 320 ktonnes per year facility in Hamburg produces 15,000 tonnes of raw acidic solution, which is then upgraded to 4,000 tonnes of 30% HCl solution, by using 400 tonnes of additives and reagents. Finally, 1,000 tonnes of solid waste (salts) has to be landfilled. Comparison with the values in Table 2 learns that the amount of solid residues is thus reduced from 8.1 kg/tonnes MSW (configuration B, salt residue) to 3.1 kg/tonne MSW (under the assumption that the MSW incinerated has a comparable composition).

This adds to the 6.9 kg/tonne MSW of filtercake, which is unchanged by this technology and which originates from the neutralisation of SO₂ and from the fly-ash, which slipped through the preceding dust removal device. The total amount of residue produced thus becomes 10.0 kg/tonne MSW combusted.

Technical feasibility

Technically, this process is feasible as it is actually practised on a large scale at several plants in Germany.

Economical feasibility

No actual data on the economical feasibility are available right now. From the fact that facilities with this technology are operated, the conclusion must be that economically the concept must be feasible. However, the processing costs at which the municipal solid waste is combusted at these plants is not known, but in general the gate fee in Germany is relatively high: around 150 EURO/tonne (on average) versus around 100 EURO/tonne (on average) in the Netherlands and even lower gate fees in other European countries. Local conditions (regulations, landfill costs and others) will have a considerable impact on the economical feasibility.

Also, the price at which the produced concentrated hydrochloric acid can be sold is obviously an important factor in this. As the hydrochloric acid market is a “saturation” market (demand and production are balanced), the price will have to be competitive or the quality has to be superior in order to successfully take over a (small) part of the market.

Other issues

One important issue in the sale of the produced hydrochloric acid is how it is classified: is it seen as a waste or as a product? This will dramatically influence the possibility to sell it and the rate at which it can be sold. The effort made to upgrade the raw acidic solution and the apparently good quality of the produced acid [Menke, 1999] would plead for classification as a product.

In Germany the situation is complicated by the fact that the “LAGA Merkblatt” ([LAGA, 1994]: a directive for the treatment of MSWC plant residues) sets limits for the impurities, which are not met by the recovered hydrochloric acid solution. For some authorities, this is reason to classify the recovered hydrochloric acid solution as a waste, pending further (legal) procedures.

One strong argument in favour of the classification as a product is the fact that, commercially available hydrochloric acid solutions do not meet the LAGA-requirements either [Menke, 1999].

Summarizing it can be stated that, in general, also in Germany, the recovered hydrochloric acid solution is considered to be a product, though some individual exceptions are still encountered [Baars, 2000].

3.2 Neutrec process

The Neutrec process was developed by Solvay and combines acid gas neutralisation by sodium bicarbonate with chemical recycling of the resulting salt residues.

Briefly, the process consists of injection of dry sodium bicarbonate without previous water injection. Compared to calcium hydroxide, which is conventionally used as reagent in classic dry or conditioned dry scrubbers, sodium bicarbonate results in a lower amount of solid residue for the following reasons:

- due to larger internal surface and higher reactivity, the required excess of additive for sodium bicarbonate can be less than for calcium hydroxide while maintaining the clean gas level below the emission limit: according to [Jacquinot, 2000] a stoichiometric ratio of 1.2 (for HCl and SO₂) would be sufficient¹;
- the sodium bicarbonate excess releases CO₂ to form Na₂CO₃;
- the formed residue components related to the adsorption of HCl (NaCl, Na₂CO₃) do not contain crystallisation water, contrary to the residue components from the addition of calcium hydroxide as CaCl₂ has one or two moles of crystallisation water.

Calculation of the mass balance under the above-mentioned conditions, learns that for the same MSW composition as for Table 2 and under stoichiometric conditions as explained above, per tonne of MSW 15.7 kg of solid residue will be produced when sodium bicarbonate is used. Comparison with the values in Table 2 learns that this is considerably less than the amounts produced in the dry and semi-dry scrubber and about the same as the total amount of solid residue produced by a wet scrubber with wastewater evaporation (configuration B).

However, flue gas cleaning is only the first step of the Neutrec process. The second step involves the purification of the flue gas cleaning residue. In this purification process the residues are first dissolved in water and filtered to separate the insoluble content (fly-ash, activated carbon and heavy metal hydroxides). The resulting brine is further purified by feeding it to a sand filter and to an activated carbon adsorption unit to adsorb any organic compounds from the brine. The spent activated carbon is recycled to the furnace for combustion. Finally, the brine is fed to columns with ion-exchange resins to remove the final traces of heavy metals. The purified brine, which consists of sodium chloride, sodium sulphate and sodium carbonate, is recycled to a sodium carbonate production plant.

Based on the same data as Table 2, the total Neutrec process thus generates a solid residue of around 2.5 kg with a moisture content of 50% (thus 1.2 kg dry matter) per tonne of MSW combusted. Comparing this to the values in Table 2 learns that

¹ According to [Jacquinot,2000] stoichiometric ratios of 1.05 for HCl and 1.3 for SO₂ are required. These are values claimed by actual operating installations, respecting the more severe emission legislation (HCl < 10 and SO₂ < 50 mg/Nm³). Here a combined value for both HCl and SO₂ of 1.2 is used.

this is the lowest amount of all configurations considered. Additionally, it should be mentioned that in contrast to the wet scrubber with wastewater discharge, which comes closest in terms of amount of solid residue produced, the Neutrec process does not discharge of wastewater to the environment.

Technical feasibility

In 1991 the first industrial scale installation provided with the flue gas cleaning technology of the Neutrec process came into operation. Since then, several other installations have installed this system.

With respect to the purification of flue gas cleaning residue and the recycling to the chemical industry, one pilot industrial plant (Rosignano, 2800 tonnes/year) is in operation and one plant (50000 tonnes/year) is under construction in France. The technical feasibility can thus be considered to be proven.

Economical feasibility

No supporting economical data considering required investments and discharge costs (or revenues) from the produced brine are (yet) available. Naturally, landfill costs are considerably reduced, but on the other hand additive costs are increased since sodium bicarbonate is much more expensive than the conventionally used calcium hydroxide: the average cost of sodium bicarbonate is more than 7 times the cost for the equivalent (same molecular reactive) amount of calcium hydroxide¹.

Partly this is compensated by the fact that the required stoichiometric ratio is considerably lower for sodium bicarbonate than for calcium hydroxide. As a result, per tonne of MSW, reagent costs for sodium bicarbonate are approximately 3 times the reagent cost for calcium hydroxide (see also [Jacquinot, 2000]). Including the reduced residue costs, the global balance for the MSWC facility is in many cases favourable to the sodium bicarbonate solution [Leitner, 2000].

So, given also the fact that existing plants are in operation, the Neutrec process must be considered economically feasible. The total costs are claimed to be in the same order of magnitude as the costs for landfill including stabilisation.

Other issues

Until now, the installed capacity for recycling of flue gas cleaning residues is limited. Extension of the capacity of the Rosignano plant to 8000 tonnes per year is presently being studied. Further plans for the future exist.

All soda plants have the potential to accept the salts from the recycling units. As a consequence, no bottleneck in processing capacity is expected. The residue purification plants will be built at the soda plant site and not at the incinerator plant, because of the lower transporting costs for flue gas cleaning residues compared to the associated larger volume of brine.

¹ According to [Jacquinot,2000] CaO costs 75 EURO/tonne and NaHCO₃ costs 190 EURO/tonne. As 1 mol CaO neutralises 2 moles HCl whereas 1 mol NaHCO₃ neutralises 1 mol HCl, per kmol equivalent acid neutralisation capacity the costs are 2.1 EURO for CaO and 16.0 EURO for NaHCO₃.

3.3 Chemical recycling of PVC with calcium chloride production

In Denmark a PVC-recycling process (on semi-technical scale) has been developed by NKT Research Center A/S. Now this process is being up scaled to a 200 tonnes per year pilot process plant. The process chemically recycles PVC waste to produce calcium chloride (for application as a road de-icing salt), a coke fraction (to be burnt), an organic condensate (to be burnt) and a metal product with high concentration of lead (50-60 wt%). The latter is the only fraction, which still has to be landfilled (as hazardous waste) and represents about 2 wt% of the initial amount of PVC to be treated.

Basically, the process consists of a reactor and a downstream separation process [NKT, 1999]. In the reactor the pre-sorted PVC (ferrous and non-ferrous is taken out as well as light plastics) is heated to moderate temperatures (maximum 375 °C) at low pressures (2-3 bar). The chlorine in PVC reacts with lime forming calcium chloride or with metals to form metal chlorides, which, depending on the type of heavy metal, are volatile or non-volatile. Part of the chlorine evades as HCl.

The gases from the reactor are led into water to absorb the HCl. The remaining gases (mainly carbon dioxide, ethane and propane) contain less than 1 wt% chlorine.

The absorbed HCl is used in the treatment of the solid residue from the reactor. This solid residue is treated in a multi-stage extraction-filtration process. By controlling pH, temperature and the amount of added water, calcium chloride and heavy metals are separated from the coke. The coke product contains less than 0.1 wt% of chlorine and lead.

In principle, the coke product as well as the remaining gases can be used in an incinerator for energy production, e.g. as steam, which is needed in the treatment of the solid residue. As mentioned before, the calcium chloride can be used as road salt and the metal residue has to be landfilled.

Presently, as far as known, this process is not (yet) suitable for the treatment of neutralisation residues. However, it may offer potential for the cleaning of neutralisation residues in the sense that heavy metals are removed from the residues. This would improve the possibilities for recycling of the neutralisation residue or at least facilitate the landfilling thereof.

3.4 Recycling of salt residue

Spray dryer residues contain soluble and insoluble salts. The soluble salts, apart from any soluble heavy metal salts, are environmentally harmless and are commonly present in (salty) water. The scope of the trials, which were executed (by

Akzo Nobel [*Middelhuis, 1999*] was to reduce the amount of flue gas cleaning residue, which ended in a C2/C3¹ landfill by:

- dissolving the spray dryer residue in water;
- precipitating any dissolved heavy metals;
- filtrating the solids; and
- discharging the solution with soluble salts into a river or sea.

The remaining solid residue (the filtercake from the filtration) with the impurities (heavy metals and fly-ash) concentrated in it, would still have to be discharged, but would be much less in volume.

The tests were executed for two types of spray dryer residues with different characteristics. The main difference was given by the insoluble fraction of the spray dryer residues: 2.8 wt% for one residue (residue A) versus 21.3 wt% for the other (residue B).

The reprocessing of the spray dryer residues showed similar differences in the resulting reduction of the volume of residue to be landfilled: 94% reduction in volume (residue A) versus 57% (for residue B).

With respect to the figures mentioned in Table 2, this means that the salt residue produced by the wet scrubber with effluent evaporation (configuration B) is reduced from 8.1 to 0.5 - 3.5 kg/tonne MSW. The total amount of residue from this configuration is reduced from 15.0 to 7.4 - 10.4 kg/tonne MSW.

Technical feasibility

The reprocessing of spray dryer residue seems technically feasible, though some bottlenecks were encountered regarding the dissolving of the residue and the filtration of the suspension. In the trials, suspended material caused unwanted precipitation in the storage tanks and clogging of the filter, resulting in relatively low filtration velocities. However, it is expected that these bottlenecks can be cleared. The resulting solution does meet the Dutch guidelines for wastewater discharge. Further research should clarify whether the results can be reproduced, also for residues from other MSWC facilities.

Economical feasibility

Based on an estimated investment for a centralized reprocessing unit for spray dryer residue the cost for reprocessing residue A were similar to the cost of landfilling without reprocessing: 100-170 EURO/tonne residue with reprocessing versus 115 EURO/tonne residue without reprocessing. For residue B the cost for reprocessing exceeded the cost without reprocessing due to the fact that more residue still had to be landfilled: 150-220 EURO/tonne residue with reprocessing versus 115 EURO/tonne residue without reprocessing.

¹ C2 and C3 are classifications for landfills used in the Netherlands: both C2 and C3 waste are hazardous wastes but C2 waste has a considerable higher leaching rate. Therefore C2 landfills have more leaching prevention measures like storage in a concrete bin. As a result, C2 landfills charge higher costs than C3 landfills.

The final decision on the economical feasibility will also depend on the measures needed to ensure the technical feasibility, also for other residues and the capacity and location of the plant.

Other issues

Finally, the feasibility will also depend on the possibilities to obtain permits for the discharge of the resulting solution and the resulting solid residues.

Obviously, this technique can only be applied to MSWC facilities equipped with a wet scrubber, where the effluent is evaporated in a spray dryer (like configuration B).

3.4.1 Special case: MSWC facility Amsterdam

The MSWC facility in Amsterdam also consists of a wet scrubbing configuration without wastewater discharge, but the design is slightly different. The main difference with respect to configuration B is the spray dryer. In AVI Amsterdam the spray dryer is actually a spray dry adsorber in which additives (lime slurry and cokes) are injected. As in other 'configuration B'-type plants, the scrubber effluent is evaporated in this spray dry adsorber, but unlike the other plants, at AVI Amsterdam this scrubber effluent also contains sulphates. Other plants usually neutralise the effluent from the alkaline scrubber with calcium (hydr)oxide, thus precipitating the sulphates as gypsum (ending up in the filtercake). At AVI Amsterdam sodium hydroxide is used and as sodium sulphate is soluble it remains solved in the scrubber effluent, which is sent to the spray dry adsorber for evaporation. As a consequence the salt residue formed is a mixture of chlorides and sulphates, plus fly-ash, cokes and excess calcium hydroxide.

In order to reduce the amount of solid salt residue, which has to be landfilled, AVI Amsterdam has developed a process for which recently a pilot plant has come into operation [Vries, 1999]. In this process the solid residue from the spray dry adsorber is solved in the (acidic) effluent from the wet scrubber. The excess of calcium hydroxide in the solid residue neutralises the acids in the scrubber effluent. Sulphates precipitate as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), chlorides remain in solution as calcium chloride. Several purification steps and filtering steps result in a filtercake consisting mainly of fly-ash and gypsum, which in dry matter roughly represents half the amount of the original residue. Besides this filtercake, through some concentration steps a 40% calcium chloride solution is obtained. This solution can be sold commercially.

Based on figures obtained from AVI Amsterdam, this process reduces the amount of solid residue from around 14 kg to around 7 kg per tonne MSW. These values are similar to the values mentioned before for the recycling of salt residue for wet scrubbers with effluent evaporation in general (as under 3.4).

In principle, this process would technically be suitable for application to the neutralisation residues from dry or semi-dry scrubbers. First, however, the technology has to be demonstrated at AVI Amsterdam.

Technical feasibility

At the moment a pilot plant has been taken into operation, which represents 25% of the required capacity for the total waste combustion capacity. This pilot plant has to demonstrate the technical feasibility.

Commercial feasibility

Economically, the investment costs are compensated by three financial benefits:

- the solid residue to be landfilled is reduced in amount and also reduced in leachability: in the Netherlands this means that it can be landfilled at lower costs (C3 instead of C2, see footnote 1);
- the resulting calcium chloride solution can be sold;
- due to the utilisation of the excess of calcium hydroxide the usage of sodium hydroxide can be reduced: as sodium hydroxide is relatively expensive, this is a considerable effect.

For AVI Amsterdam the process is economically feasible from the saving of the landfill cost and the saving of the cost for sodium hydroxide alone. A revenue from the sale of calcium chloride obviously improves the feasibility but is not required to cover the cost. At other facilities, which use less sodium hydroxide (which normally is the case), the financial gain in reduction of additive costs is much less. For these facilities the calcium chloride solution must create a considerable revenue to maintain the economical feasibility. When the saving of additive costs is neglected, the required revenue for the calcium chloride solution to maintain economical feasibility, should be at least 20-25 EURO per tonne. Since the calcium chloride market is saturated (displacement market), getting this revenue may not be easy.

Other issues

AVI Amsterdam has patented this process (Dutch patent granted [Vries, 1999], European patent pending). Several licences have already been sold [Vries, 2000].

3.5 Reconstruction of the flue gas cleaning system

As can be seen in chapter 2 and in [Rijkema, 1999] the type of flue gas cleaning has a large impact on the amount of solid neutralisation residues, which is generated. However, as the amount of residue generated is not the only factor in the decision which configuration should be implemented, other configurations, which generate more solid neutralisation residues per tonne of waste combusted than configuration A (chapter 2), are built as well.

In the Netherlands only wet scrubbing systems are in operation, either with wastewater discharge (configuration A) or with wastewater evaporation in a spray dryer (configuration B). The main reason for applying configuration B instead of A is that the facility cannot (not close to suitable surface water) or does not want to discharge of (cleaned) wastewater to surface water, because of the negative public perception of wastewater discharge. The fear for a negative public perception played a role in the decision of the MSWC facility in Alkmaar for a wastewater free operation of the scrubbers, although the facility is relatively close to the sea. Legally, in the Netherlands there is no objection to the discharge of wastewater, provided that [*Saft, 1997*]:

- the amount of other polluting components than salts is within limits: the wastewater purification, which is currently applied at the MSWC facilities is largely sufficient to comply with the standards (this purification consists of neutralisation, flocculation, precipitation and sedimentation followed by filtration of the resulting effluent by a sandfilter and an active cokes filter);
- the receiving surface water is large enough (this also is the case for all the facilities, which discharge of cleaned wastewater).

For the facilities, which have configuration B, a study has been made [*Galavazi, 1998*] on the possibilities to change the flue gas cleaning configuration in such a sense that no longer a solid neutralisation residue is generated. Instead a concentrated CaCl_2 -solution, gypsum and a filtercake are produced.

In general, the adjustment of the flue gas cleaning system consists of the following measures:

- stop the evaporation of the wastewater in the spray dryer;
- keep the effluents from the first and second scrubbing step separate;
- discharge of the sulphates as gypsum;
- add a concentrating step for the chlorides solution to concentrate it up to 25 wt%;
- adjust the wastewater cleaning section to clean the chlorides solution;
- transport the concentrated chlorides solution.

For the concentrated chlorides solution in principle two options are open: recycling or discharge into suitable surface water. As recycling options for concentrated CaCl_2 -solutions are not very likely to be found, the best option is to discharge into a river or a sea [*Galavazi, 1998*]. In this scenario the concentrating step serves as a way to reduce transport costs of the salt solution.

The adjustments made are schematically represented in Figure 2.

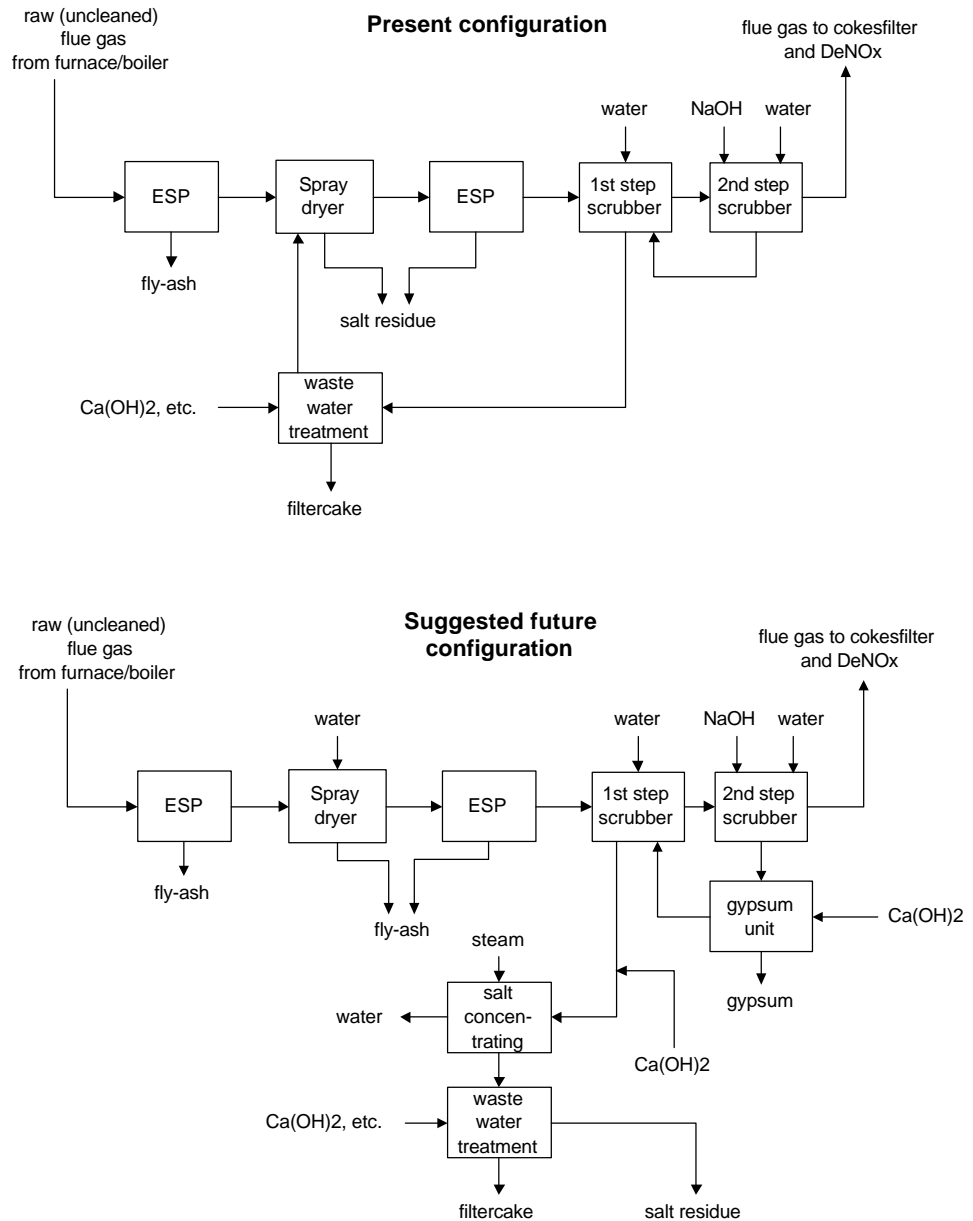


Figure 2 Adjustment of the flue gas cleaning configuration (configuration B from chapter 2) to reduce the amount of solid residues generated.

Through these adjustments the amount of solid residue, which remains from the salt residue, is only 3 to 6% of the original amount: from 8.1 to 0.24 - 0.49 kg/tonne MSW. The total amount of solid residue (including filtercake) for a wet scrubber with wastewater evaporation (configuration B) is thus reduced from 15.0 (see Table 2) to 7.2 - 7.4 kg/tonne MSW.

Technical feasibility

Technically, the presented solution is feasible in general. However, Figure 2 represents a general picture and per plant small differences may occur. Therefore, each MSWC plant must be looked into in detail to make a definitive judgement of the feasibility per plant.

Economical feasibility

For 4 Dutch facilities the general economical consequences were estimated [Galavazi, 1998]. Per facility, investments ranged from 1.4 - 2.3 to 2.3 - 4.5 million EURO, dependent on the capacity of the facility. The capital cost, as well as the other costs can, however, easily be financed from the reduction of the landfill cost. For the 4 facilities, which were investigated, the annual saving, including all costs, ranged from 160,000 to 680,000 EURO. Therefore, generally spoken, this technology is economically feasible. A detailed study per MSWC facility will have to be carried out to know the exact cost savings.

Other issues

Like for the recycling of the salt residue, as discussed in section 3.4, the feasibility of this technology largely depends on the possibility to discharge of salty water to surface water, without (considerable) costs. If permits for this discharge cannot be obtained, the salt solution has to be evaporated to produce calcium chloride, an option which (for the Netherlands) is not perceived to be cost-effective [Galavazi, 1998].

3.6 Immobilisation and washing techniques

To decrease the leachability of the neutralisation residues immobilisation and washing processes can be applied. The technology presented in chapter 3.4 and 3.4.1 also represent a special case of a washing process. For this special process reference to these chapters is made: here washing processes are discussed more in general.

A good overview of possible processes for flue gas cleaning residues from MSWC is given (among others) in [Flyvbjerg, 1997] and [BUWAL, 1998]¹. In principle these techniques can be subdivided in (as in [Krüger, 1996]):

- immobilisation with cement, eventually with chemical stabilisation;
- hydrometallurgical (washing) processes;
- low temperature pyrometallurgical processes;
- high temperature pyrometallurgical processes.

In the low temperature pyrometallurgical process the solids are heated to 350 - 600 °C with the only objective to destroy PCDD/F² (and other organic components). As this is not reducing the amount of residue or further improving the quality of the residue, this technique is not further discussed here. High temperature pyrometallurgical processes are aimed at the production of an inert (= non-leaching) solid material of improved quality and are further discussed below.

Immobilisation with cement

Immobilisation with cement is a commonly applied technique. By doing so the fine neutralisation residues are bound together and water (for leaching) can hardly percolate any more which drastically reduces the leachability. Instead of cement other solidification materials like coal fly ash, cement kiln dust and blast furnace slag can be used as long as the overall mixture contains sufficient concentrations of SiO₂ and Al₂O₃ in combination with lime [Whiting, 1997].

Other ways of immobilisation (not common) are by applying phosphates or sulphides. These chemical immobilisation techniques are based on the formation of insoluble compounds or complexes in which heavy metals (especially lead and cadmium and to a lesser extent copper and zinc) are strongly bound. Usually, these immobilisation techniques are applied to facilitate the landfilling of the solid residue. In some occasions it enables the use of the solid residue as a construction material. Examples of commercially available chemical treatment processes can be found in the United States and in France [Whiting, 1997].

According to a questionnaire among European MSWC facilities over two-thirds of the facilities applies stabilisation techniques for their “APC residues” [Juniper, 1998]. However, as in this questionnaire “APC residues” includes fly-ash no clear picture on the application of stabilisation techniques to neutralisation residues is available.

¹ In literature, presented processes often deal with specific residues, hardly ever all the residues which are produced are considered. In [Flyvbjerg, 1997] salt residues from evaporation of cleaned wastewater (salt residue in configuration B) are not taken into account: the report focuses on neutralisation residues from dry and semi-dry scrubbers (configurations C and D in Figure 1) and on the filtercake produced by a wet scrubber (like the filtercake in configuration B; see footnote ² on page 7). [BUWAL, 1998] only considers a mixture of fly-ash and filtercake (in a typical ration of 80/20) as the residue to be treated, since in Switzerland no dry or semi-dry scrubbers or spray dryers are in operation.

² PCDD/F = poly-chlorinated-dibenzo-para-dioxins and -furans

Hydrometallurgical processes

Washing processes have been developed, especially for bottom-ashes and fly-ash. The principle is always the same: by washing, usually with an acidic solution (for which often the effluent of the first scrubber step is used), heavy metals and soluble salts are leached out, so that the remaining solid residue has a strongly reduced leaching potential and can be reused (for roads or construction purposes). Heavy metals can be concentrated in a filtercake, which may be reused in the metal industry, depending among others on the metal content.

Upon washing of the solid neutralisation residues from dry and semi-dry processes around 30 - 40% of the mass is reduced as these contain relatively large amounts of soluble salts (mainly CaCl_2) [Flyvbjerg, 1997]. As a consequence the remaining solid residues can be landfilled more easily, i.e. in a cheaper landfill class. On the other hand the effluent, containing salts and heavy metals, still has to be cleaned in a wastewater cleaning facility to precipitate the heavy metals and the resulting cleaned effluent must be discharged or evaporated to produce salts for recycling or controlled landfill.

High temperature pyrometallurgical processes

The last method for immobilisation is thermal treatment: by heating the residues to elevated temperatures (1500 – 2000 °C) melting and slagging occurs. By addition of reducing agents to the melting processes, heavy metals are transferred from oxides or chlorides to their pure metal form and can be separated as molten metals by draining from the oven. These metals can be reused in the metal industry. After cooling, the remaining solid residue is a glass-like residue, which with respect to leaching can practically be considered inert.

Until now, thermal stabilisation is not practised on a large scale due to the relatively high energy costs and the relatively high complexity and less proven status of the technology. In addition, legislation, as yet, does not require the greater degree of stabilisation provided by thermal stabilisation compared to other immobilisation techniques [Juniper, 1998]. Experiences with thermal stabilisation (like from the USA, Japan and Switzerland) are usually restricted to fly-ash and maybe some filtercake, but not the neutralisation residues of dry and semi-dry scrubbers [Flyvbjerg, 1997; BUWAL, 1998]. A list of ash vitrification processes is given in [Whiting, 1997] but, here too, it is unclear whether these processes apply to fly-ash only or that neutralisation residues can also be dealt with.

Technical feasibility

Immobilisation with cement can be considered proven technology for fly-ash and filtercake [BUWAL, 1998]. In Belgium (Wallonia), France and Italy, cement stabilisation of neutralisation residues is required before these residues can be landfilled [Jacquinot, 2000]. Therefore, this technique can be considered proven technology as well. For neutralisation residues immobilisation with cement can best be preceded by a washing process to remove the soluble salts. Further leachate reduction

can be achieved by chemical immobilisation. However, little experience with cement immobilisation of **neutralisation** residues is reported in literature. Washing processes are mainly applied to fly-ashes as washing of neutralisation residues only solves part of the problem. Specific exceptions are given by the development as presented in chapters 3.4 and 3.4.1.

High temperature immobilisation is close to being considered proven technology since ample experience is available from other industries (especially the metal industry) and processes are offered commercially. This mainly concerns the melting of fly-ashes [BUWAL, 1998]. For filtercake and neutralisation residues this is not (yet) the case.

Economical feasibility

With respect to the cost of the mentioned immobilisation and washing techniques not much data is available and very often it is unclear whether the mentioned costs apply to fly-ash only or to all flue gas cleaning residues including neutralisation residues.

In general, the cost for stabilisation of the residues is estimated at 70 EURO per tonne of solid neutralisation residue [Jacquinot, 2000]. Other sources report a cost of 95 - 130 EURO/tonne for stabilisation including chemical immobilisation [Whiting, 1997]. In Switzerland the cost for immobilisation with cement, but also for washing of the residues with an acidic solution is found to be competitive (on a cost basis) with the present way of disposal: landfilling in (salt)mines [BUWAL, 1998]. Figures mentioned are 250 to 290 EURO per tonne of residue.

Thermal treatment of the solid residue is more expensive. Costs reported differ considerably between sources: e.g. 160 - 320 EURO per tonne [Whiting, 1997] and 320 - 950 EURO per tonne residue [BUWAL, 1998]. Especially for thermal treatment, processing in a central unit offers many energetic and thus financial advantages: e.g. according to [BUWAL, 1998] the maximum cost of thermal treatment is reduced from the previously mentioned 950 EURO per tonne to 480 EURO per tonne if central, larger units are applied.

3.7 Other technologies

In this chapter some other technologies, which are currently being developed will be briefly discussed. In general, the present potential of these processes to decrease the amount of neutralisation residue from MSWC to be landfilled is limited. Nevertheless, these technologies represent interesting ideas and are worth mentioning here.

3.7.1 NaCl production

NaCl (table or kitchen salt) can be produced from the scrubber effluent of the acidic scrubber. In fact, this is a variation on the process, which produces concentrated hydrochloric acid (see 3.1). By neutralisation of the HCl-solution with sodiumhydroxide (NaOH) the NaCl is produced. After the necessary purification steps, the resulting liquid can be evaporated to cause crystallisation of solid salt [Lemann, 1998].

The reuse of the produced table salt is not easily achieved. The quality of the salt appears to be insufficient for usage in the chloralkali electrolysis process (production of Cl_2 and NaOH from NaCl). Therefore it has to be diluted with natural salt [Enders, 1991]. However, in this process per kg of NaCl, 0.61 kg of Cl_2 and 0.68 kg of NaOH is produced. The use of NaOH to neutralise HCl to NaCl is then only sensible when there is a need for Cl_2 . In general, this appears not to be the case [Enders, 1991; Faulstich, 1991], which decreases the attractiveness of this way of treatment considerably.

Another option is to deliver the NaCl to soda ash plants. However, there it will result in an equal flow of residual CaCl_2 for which there is no market either [Faulstich, 1991].

All together, the production of NaCl from acidic scrubber effluent does not seem to be feasible, in general. Some MSWC plants (2 in Germany), however, have found a niche market to dispose of the solid NaCl they produce [Faulstich, 1991]. By doing so, they have considerably reduced the amount of solid residue to be landfilled, comparable the reduction in landfill volume realised by the technologies as discussed in chapters 3.1, 3.4 and 3.5.

3.7.2 Taiheiyo cement corporation

At the Taiheiyo cement corporation a recycle system has been developed for ashes from MSWC facilities. This system converts bottom-ash, fly-ash and neutralisation residues into material, which can be used in cement kilns.

In Japan, the fly-ash is usually collected together with the neutralisation residues in a dry scrubber as in contrast to European MSWC facilities this dry scrubber is not preceded by a dust removal device. As a consequence the neutralisation residue is not comparable to the residue produced at European MSWC facilities: the (inert) ash fraction is much larger.

In the developed process, both the bottom-ash and the fly-ash / neutralisation residue mixture (the residue from the dry scrubber) are washed with water to remove the highly leachable chlorides from the ashes. The insoluble part is fed to the cement kiln together with the bottom and fly-ash, substituting (for a small part) limestone. The wastewater is then cleaned in a wastewater purification system, among

other by blowing CO₂-rich kiln exhaust gas in the reaction tank before precipitation occurs. This enhances the precipitation of heavy metals [Taiheiyo, 2000]. The filtercake produced in the wastewater cleaning process is fed to the cement kiln if the heavy metal content is below the acceptance levels. If this filtercake contains too much heavy metals it must be treated further. This further treatment is presently being studied in a pilot plant.

The cleaned wastewater is led into the municipal sewage system.

The process is applied to existing cement kilns and will be applied to a newly built cement plant with a capacity of 100,000 tonnes per year and will come into operation in the spring of 2001. At this new plant metals will be recovered for recycling at a metal smelter in Japan [Taiheiyo, 2000].

3.7.3 The TREFID process

The TREFID process separates residues from dry and semi-dry scrubbers (which used a lime based sorbents). The main resulting fraction from this separation is an inert fraction (approximately 70 wt% of the input) which mainly consists of oxides, and can be used in cement kilns. Besides this main fraction a sodium and calcium chlorides fraction (approx. 25 wt%) and a fraction with heavy metal hydroxides is produced. The process involves a number of steps consisting of washing, soda contacting and filtering.

At present, a small pilot is running (20 kg/hr) and a larger plant (1 tonne per hour) is being planned [Gloriod, 2000].

3.7.4 The CT-Fluapur process

The CT-Fluapur process intends to clean fly-ash by evaporating the heavy metals from the fly-ash. By heating the heavy metals to around 900 °C in a flue gas atmosphere enriched with hydrochloric acid, the heavy metals are volatilised (as chlorides) from the fly-ash. Then the heavy metals are condensated on a filter to form a concentrated heavy metal mixture, which may be recycled. The remaining fly-ash thus has become practically inert and can be used as a sand-like construction material [Jakob, 1999].

Until now, the process has been demonstrated in a laboratory scale fluidised bed. The process can be integrated with existing MSWC facilities as it combines heat, fly-ash and hydrochloric acid, which can be made available at a MSWC facility. The filtered flue gases from the Fluapur process can then be treated further in the flue gas cleaning system of the MSWC facility [Jakob, 1999]. Until now, investigations were restricted to fly-ash and no neutralisation residues were involved.

3.7.5 Recupyl

The process developed by Recupyl consists of a combination of a hydrometallurgical pre-treatment of the residues followed by a vitrification process by using a plasma torch. The hydrometallurgical pre-treatment enables the recovery of heavy metals and salts, which might be led back to industry for re-utilisation (e.g. electrolytic recovery of Zn). The final product, a vitrified slag, is a glass-like material, which as such can be used as a construction material [Recupyl, 2000].

Two products exist:

- REFIOM: Résidus d'Épuration des Fumées d'Incineration d'Ordures Ménagères (flue gas cleaning residues from municipal waste combustion);
- REFIDI: Résidus d'Épuration des Fumées d'Incineration des Déchêts Industriels (flue gas cleaning residues from the combustion of industrial wastes).

The Recupyl process can be applied to several ash compositions and has been demonstrated on a pre-industrial scale. The process is applied at one MSWC facility in France, which combusts 120 ktonnes of MSW per year, producing 3500 tonnes of REFIOM [Recupyl, 2000].

4. Evaluation and conclusions

First the main characteristics of the technologies as discussed in chapters 3.1 to 3.5 are summarized in Table 3. The chemical recycling of the neutralisation residue as discussed in 3.3 is left out of consideration, since this cannot be applied to MSWC residues yet.

Comparing the characteristics of the different technologies, as presented in Table 3, one of the first things, which catches the eye is that 4 out of the 5 mentioned technologies can be applied to MSWC facilities, which have a wet scrubber with effluent evaporation (configuration B). The main reason for this is the production of a mainly Cl-salts based residue separately from the production of a filtercake containing gypsum and heavy metals. This filtercake is not touched by any of the techniques: only the salt residue (see Figure 1). As a consequence the minimum amount of solid residue to be landfilled is 6.9 kg/tonne MSW for these technologies as this is the amount of filtercake produced (see Table 2).

The reasons why the filtercake is not subject for further treatment is not looked into in this report but briefly this has to do with the poor marketability of the gypsum, which may produced from this filtercake. The gypsum demand is (largely) exceeded by the supply, which makes competition very tough. This competitive position is worsened by the relatively large effort required (as gypsum is hardly soluble in water, purification, to decrease the heavy metal content, is not easy) to obtain a competitive quality to e.g. gypsum from coal-fired power plants. As a result, the recycling of the filtercake is hardly ever tried.

For the salts residue, purification is less difficult, because the Cl-salts are soluble in water. The products, however, also suffer from a limited market potential. For calcium chloride the best what can be achieved (economically) seems to be the disposal at zero costs in suitable surface water. The hydrochloric acid produced is a product with good enough quality to be competitive on a market where there is enough supply to meet demand. However, the effort required for upgrading is considerable and does produce some solid residue.

Which of these options is to be preferred depends on the circumstances. The two most important issues in a decision between the two options, hydrochloric acid or calcium chloride, are:

- the possibility (geographically as well as legally) to discharge of a cleaned calcium chloride solution;
- the possibility to set up contracts for a long enough period for the sale of the produced hydrochloric acid.

Table 3 Characteristics of discussed technologies for reduction of the amount of MSWC residue to be landfilled (see text).

Technology	Commercial products	Status of development	Solid residue to be landfills [kg/tonne MSW combusted]	% reduction of residue to be landfilled ^{1,2}	Economical feasibility	Technical feasibility	Comments ²
Production of hydrochloric acid (chapter 3.1)	Concentrated hydrochloric acid (15 – 30 wt%)	5 plants in operation, 3 under construction (all in Germany)	10	33% (B) -294% (A)	Yes, proven	Yes, proven	Applicable to wet scrubber systems only, sensible for B. Market potential for HCl acid limited. Filtercake (SO ₂ related) not touched.
Neutrec process (chapter 3.2)	Feedstock for soda plant	- Scrubbers (approx. 20) in operation since 1991 - Recycling of residue: 1 industrial pilot plant in operation; more capacity planned	³ 1.2 (dry matter)	³ 94% (C) 95% (D)	Yes, indicated	Yes, proven	Applicable as a retrofit to C and D. Recycling capacity yet to be extended, but not seen as a limiting factor.
Recycling of salt residue (chapter 3.4)	Calcium chloride	Pilot plant experiments executed	7.4 to 10.4	31 to 51% (B)	Yes, possibly	Yes, probably	No market for calcium chloride expected: discharge in surface water? Applicable to B. Filtercake (SO ₂ related) not touched.
Recycling of salt residue: special case (chapter 3.4.1)	Calcium chloride	Industrial pilot plant just started operation	7.0	~ 50% (B) ~ 65% (C) ~ 72% (D)	Yes, in this special case	To be demonstrated by pilot plant	Special case: revenue from CaCl ₂ not necessary: discharge in surface water? Applicable to B. May be also applicable to C and D. Filtercake (SO ₂ related) not touched.
Adjustment of flue gas cleaning system (chapter 3.5)	Calcium chloride	Concept, composed of existing technology	7.2 to 7.4	51 to 52% (B)	Yes, probably	Yes, probably	Applicable to B only. Market for CaCl ₂ not needed: discharge in surface water? Filtercake (SO ₂ related) not touched.

¹ The percentage reduction is indicative and is specified relative to flue gas cleaning configurations as given in Figure 1 with the amounts of solid residues produced as specified in Table 1. A negative value indicates an increase of the amount to be landfilled.

² The configurations are indicated by letters: A = wet scrubber with effluent discharge, B = wet scrubber with effluent evaporation, C = semi-dry scrubber and D = dry scrubber.

³ The amount given includes the recycling of the flue gas cleaning residue. Without that (just application of a dry scrubber operated with sodium bicarbonate) the amount of residue to be landfilled is 15.7 kg per tonne MSW combusted and the percentages in reduction of landfill volume drop to 23% (C) and 38% (D).

For the other flue gas cleaning configurations, which were considered in this study, the options for reducing the amount of solid residues to be landfilled are limited. For the wet scrubber, which separately discharges, of two cleaned effluents (configuration A) this is obvious: the amounts to be landfilled are very low already. For the dry and semi-dry scrubber this seems to be due to the complexity of the produced residue: by adsorbing all the pollutants from the flue gas in one step the resulting residue is a mixture of components. Alternative treatment for fractions of these residues requires separation, which is labour-intensive and as a consequence quite costly. Moreover, experience from other technologies learns that the marketing of the products of such treatment is extremely difficult. Together this may explain why attempts to treat the residues of dry and semi-dry scrubbers, until now, have not been so numerous and not so successful.

As an exception to this, the Neutrec process offers an interesting alternative with good market potential with respect to the recycling of the products. The remaining amount of residue to be landfilled is extremely low. Drawbacks for this process for existing facilities may be found in the necessity to switch the use of the additive in the scrubbers: from calcium hydroxide (most common) to sodium bicarbonate. Though at present, no limitations in the acceptance of the product at soda plants is foreseen, it is not clear whether there may arise problems when (many) more facilities will implement the Neutrec process. The lack of installations, which can purify and upgrade the scrubber residue, must be seen as a temporary restriction to the technology, though on the other hand, the erection of such installations does require considerable effort and will not be realised overnight.

The process, which is being tested in a pilot-plant at AVI Amsterdam, might offer a solution for the neutralisation residues from dry and semi-dry scrubbers. However, this would require testing first and on beforehand the economical feasibility for dry and semi-dry scrubbers is not favourable.

Among the other technologies, which were mentioned in much less detail, the most interesting technologies are the TREFID, process and the process offered by Taiheiyo. Both apply to the residues of dry scrubbers and both have the cement oven as the final recipient for the produced materials.

The TREFID process, however, is in one of the first stages of development and much will depend on the demonstration of the process on a larger scale.

The process by Taiheiyo is designed for the Japanese situation at MSWC facilities but is expected to be applicable for the European situation as well.

For both technologies (TREFID and Taiheiyo) it will be very important to know to what extent cement kilns can or will accept the produced materials.

The production of sodium chloride is a proven technology but the (current) market potential is low.

The CT-Fluapur process and the RECUPYL process might have potential to play a role in the treatment of neutralisation residues. The CT-Fluapur process, however, still is in a very early stage of development and it is still too early to judge the potential properly, especially because it has not been applied to neutralisation residues yet (only to fly-ash). The RECUPYL process is much more mature as the process is already implemented at one facility. However, information on the process is scarce until now and here also it is uncertain whether the process can be applied to neutralisation residues.

Both the CT-Fluapur and the RECUPYL process can be regarded as processes with the primary objective to improve the quality of the residues, which eventually may lead to a decrease in the volume of residue to be landfilled.

Finally, among the processes, which are intended to decrease the leachability of the residues instead reducing the amount produced, immobilisation plays a dominant role (for now). Washing processes and vitrification processes are being developed but generate aqueous waste streams (washing techniques) or require a lot of energy (vitrification). Many of these technologies are only applied to fly-ashes yet: the treatment of neutralisation residues is more complex and thus many times processes must prove to be successful for fly-ash before they can be adapted to more complex residues like neutralisation residues.

Compared to the other techniques, immobilisation is relatively simple. As long as neither markets exist for produced materials nor regulations, which require the inertisation of the residues, for the time being the simplest (the cheapest) technology prevails. This preference for immobilisation is further enhanced by legislation (like in a few countries) requiring immobilisation prior to landfilling.

Economical feasibility

One general remark concerning the economics of the presented situation must be made. Though for almost each presented technology a case can be presented where the process is economically feasible, this is not universally valid. On the contrary, for each separate situation other conditions may apply, which will require renewed determination of the economical situation.

An example is given by the AVI Amsterdam facility where the economical feasibility of the presented technology is improved by a cost saving for sodium hydroxide, which for historical reasons was needed at this plant. For other plants, which can do without this sodium hydroxide due to a different process configuration, the economical picture of the presented technology is a lot less favourable.

Another example is given by the difference in cost of landfill against which the economical feasibility is determined. These landfill cost may range from under 100 to over 300 EURO per tonne.

4.1 Conclusions

- The 5 most promising technologies, for reducing the amount of neutralisation residue to be landfilled, were looked into in detail. These technologies are:
 - = Production of hydrochloric acid;
 - = Neutrec process;
 - = Recycling of salt residue;
 - = Recycling of salt residue: special case (AVI Amsterdam);
 - = Adjustment of flue gas cleaning system.Other technologies were only briefly discussed.

- The majority of the 5 considered technologies apply to MSWC facilities, which have a wet scrubber with wastewater evaporation (configuration B). Between the two separately produced residues in this configuration, the efforts to reduce the amount of residue to be landfilled are restricted to the chlorine salt containing residue whereas the gypsum based filtercake is left untouched. By these technologies, the amount of residues, which remains for landfilling, is reduced by approximately 50%.

- Among the 5 technologies considered, the production of hydrochloric acid and the Neutrec process can rely on existing facilities as a reference and on an existing market for their products. The other 3 technologies considered produce calcium chloride as a product. The marketability of calcium chloride, however, is poor and the success of the proposed technology depends on the possibility to discharge of the calcium chloride into surface water (at little or zero costs). Besides technical arguments, politics and public opinion will play a role in this issue.

- Of the considered technologies the Neutrec process realises the largest reduction of the amount of solid residues, which still has to be landfilled. This is the only technology, which results in (slightly) less solid residues than for a wet scrubber with separate discharge of scrubber effluents (configuration A). This demonstrates that the impact of the type of flue gas cleaning configuration highly influences the amount of solid residue produced.

- Other interesting technologies, which in future might contribute to the treatment of neutralisation residues, are the process by Taiheiyo cement corporation and the TREFID process. Both use their products of treating the neutralisation residues for recycling in the cement process.

- Improvement of the quality of the residue (decreasing the leachability) is most often applied by immobilisation techniques, most commonly with cement or cement-like waste materials or by-products. Vitrification and washing processes are technically feasible for fly-ash, but for neutralisation residues they are hardly ever applied (yet).

- Though processes can be economically feasible for a certain plant, for each other plant this has to be redetermined individually, as many differences in circumstances between facilities are of influence.

5. Literature references

- [1] Baars, 2000
Personal communication with Dr. Bodo A. Baars, May 2000.
- [2] BUWAL, 1998
Die Rückstände der Verbrennung. Flugasche und Filterkuchen.
Umwelt-Materialien Documents Nr. 100, 1998.
- [3] Cousin, 1993
Möglichkeiten und Grenzen der Gewinnung und Verwertung von Salzsäure
aus Abfallverbrennungsanlagen.
R. Cousin
Abfallwirtschaftsjournal 5 (1993), Nr. 10, 759-768.
- [4] Enders, 1991
NaCl aus Abfallverbrennungsanlagen
R. Enders, C. Vater, M. Jekel
Müll und Abfall, Heft 8, 1991, S. 482 – 490.
- [5] Faulstich, 1991
Wertstoffgewinnung aus Rückständen der Abfallverbrennung und
Rauchgasreinigung.
M. Faulstich, A. Freudenberg, G. Kley, P. Köcher
Abfallwirtschaftsjournal 3 (1991), Nr. 6, S. 339 – 345.
- [6] Flyvbjerg, 1997
Restprodukter fra roggasrensning ved affaldsforbrænding 3.
J. Flyvbjerg, O. Hjelmar
Arbejdsrapport fra Miljøstyrelsen, Nr. 92, 1997.
- [7] Galavazi, 1998
Presentation at the meeting for re-use of flue gas cleaning residues,
organised by the Center for Advice on MSWC Residues (Adviescentrum
AVI-Reststoffen).
R. Galavazi
Utrecht, 9 april 1998.
- [8] Gloriod, 2000
Information obtained from Pierre Gloriod, May 2000.

- [9] Jacquinot, 2000
The influence of PVC on the quantity and hazardousness of flue gas residues from incineration.
B. Jacquinot, O. Hjelmar, J. Vehlow
Report for the EU commission, April 2000.
- [10] Jakob, 1999
Removal of heavy metals from Municipal Solid Waste Incinerator Fly-ash: the CT-Fluapur Process.
A. Jakob, R. Moergeli
R'99 Proceedings, Vol. II, p. 182-186, 1999.
- [11] Juniper, 1998
Waste-to-Energy. Trends in Europe. 3rd Biennial Industry Survey.
T. Appel
Juniper Consultancy Services Ltd, Gloucestershire, United Kingdom, September 1998.
- [12] Krüger, 1996
Wertstoffgewinnung aus Filterstäuben der Abfallverbrennung.
J. Krüger, G. Grund, E. Rombach
Abfallwirtschaftsjournal 6/96, 28-36.
- [13] Kürzinger, 1997
Stand der Rauchgasreinigung von thermischen Abfallverwertungsanlagen.
K. Kürzinger, E. Thomé
Müll und Abfall 3, 1997, 126-130.
- [14] LAGA, 1994
Merkblatt Entsorgung von Abfällen aus Verbrennungsanlagen für Siedlungsabfälle, verabschiedet durch die Länderarbeitsgemeinschaft Abfall
- [15] Leitner, 2000
Personal communication with H. Leitner, Solvay, June 2000.
- [16] Lemann, 1998
PVC thermisch entsorgen.
M. Lemann
Umwelt Bd. 28 (1998), Nr. 3, March.
- [17] Menke, 1999
Salzsäure aus Müllverbrennungsanlagen: Product oder Abfall?
D. Menke, B.A. Baars, H. Fiedler
Müll und Abfall 8, 1999, 490-495.

- [18] Middelhuis, 1999
Opwerking van AVI Restzouten. Resultaten van pilot plant proeven.
(Refinement of MSWC salt residues. Results of pilot-scale tests. In Dutch)
B.J. Middelhuis
Akzo Nobel Research Report, RT F99234/BM/ae, August 1999.
- [19] Recupyl, 2000
Le procédé de traitement des REFIOM et des REFIDI.
<http://perso.wanadoo.fr/recupyl/RECUPYL.html>
March 2000.
- [20] Rijpkema, 1999
PVC and municipal solid waste combustion: Burden or benefit?
L.P.M. Rijpkema
TNO-report R99/462, December 1999.
- [21] Saft, 1997
Lozen AVI-Rookgasreiniging-zouten op oppervlaktewater (Discharge of
MSWC flue gas cleaning effluents/salts to surface water, in Dutch).
R.J. Saft
Letter from the Institute for Inland Water Management and Wastewater
Treatment to the PVC Steering Group dated 21/4/1997.
- [22] Taiheiyo, 2000
The Recycle Process of Incinerator Ash from Urban Waste.
Information brochure by Taiheiyo Cement, 2000.
Including personal communication (E-mail) with Y. Yasuda, June, 2000.
- [23] Vries, 1999
Werkwijze en inrichting voor het opwerken van een rookgasreinigingsresidu.
(Method of operation and facility layout for upgrading a flue gas cleaning
residue, in Dutch).
C. de Vries
Dutch Patent NL C1006515, March 1999.
- [24] Vries, 2000
Personal communication with C. de Vries and W. Sierhuis, GDA (AVI
Amsterdam), 25 April 2000.
- [25] Whiting, 1997
Management of Ash Residues From Waste-to-Energy Processes: An
overview of Current Practices in Europe & Technical Alternatives.
K.J. Whiting
Waste-to-Energy Conference, Copenhagen, Denmark, 4/5 December 1997.

6. Authentication

Name and address of the principal:

ECVM
Attn. Mr. J.P. De Grève
Av. E. van Nieuwenhuysse 4, Box 4
B-1160 BRUSSELS
Belgium

Names and functions of the cooperators:

L.P.M. Rijpkema

Names and establishments to which part of the research was put out to contract:

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Date upon which, or period in which, the research took place:

November 1999 – June 2000

Signature:

Approved by:

L.P.M. Rijpkema
project leader

S. van Loo
head of department