ISWA Position Paper on handling of APC residues

1. Introduction
ISWA has a new report on the Management of Air Pollution Control (APC) Residues from Waste-to-Energy (W-t-E) Plants—An overview of important management options covering Europe, Japan as ISWA countries by the ISWA Working Group on Thermal Treatment of Waste. The report will be published as soon as printed and will be sent to the Commission. The draft of the report has been submitted as input to the work done on the BREF incineration document.

The Report is presenting the state-of-the-Art and future options on the handling of flues cleaning residues plants from W-t-E for recovery or disposal. The techniques selected are currently used, or are well documented.

The ISWA Working Group on Thermal Treatment is not at the moment able to give a clear position on the Best Available Technology (BAT). There are some new solutions which we do not know enough about to state that these are to be used. The ISWA Working Group on Thermal Treatment has a subgroup dealing with this issue, which will follow the development and at a later stage form a more clear position on the BAT.

2. What are APC residues
The APC residues are in general high polluted by heavy metals, salts and other e.g. organic contaminants which are classified as hazardous waste. To avoid negative environmental impact the residues have to be handled or treated in a special way.

In this paper, APC residues are defined to include all solid residues produced in or after the heat recovery systems (boiler/economizer): fly ash, boiler ash, excess lime and reaction products (dry/semidry), sludge from scrubber solution treatment and gypsum (wet).

- There are two main types of air cleaning systems, dry/semidry and wet systems. The quality of residues is varying depending on e.g. temperature and additives.
- The report deals with the following options
  - recovery and utilisation
  - solidification
  - thermal treatment
  - extraction and separation
  - chemical stabilization
  - landfilling options

3. How to handle APC residues:
If possible it is preferred to recycle the residues into products e.g. salts, gypsum and filler material for salt mines, but present only a small part is recovered and for the remaining part no sustainable and economical feasible methods of reutilization are available. If it is not possible to recover then disposal is necessary. Landfilling is the most important environmental concern. Leaching of heavy metals and salts is the main problem.
Attempts have been made to use the APC in construction, however this has been carried out in full scale, but from an environmental point of view it can be viewed as disposal. It is important to stress that all kinds of available treatment options include some kind of landfilling or storage of solid residue.

The main goal today is to minimise the long-term release of leaching of primary heavy metals. The interesting parameter when comparing methods are how well they reduce leaching from the final treated product and how much energy and resources they use in the treatment process. Treated or untreated residues can potentially continue leaching/releasing heavy metals but in any case less than the content of the input for centuries and likely millennia. Treatment technologies incl. extraction of heavy metals can substantially reduce the amount of heavy metals available for leaching.

When comparing costs of various methods it is important to know if the cost for landfilling is included as it is in underground landfilling or not. See an estimate over costs below however, it should be noted that costs estimates are associated with significant uncertainties and can only be used as guidance!

Table 1 Estimated costs of different processes for APC residues treatment including change of weight and recovery potential

<table>
<thead>
<tr>
<th>Process</th>
<th>Change of weight, %</th>
<th>Recovery potential</th>
<th>Estimated cost per ton of residue, €</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement solidification</td>
<td>+20-50</td>
<td>yes</td>
<td>25-50</td>
</tr>
<tr>
<td>Vitrification</td>
<td>+30-50?</td>
<td>only in special cases</td>
<td>100-500</td>
</tr>
<tr>
<td>Melting</td>
<td>no</td>
<td>“</td>
<td>100-500</td>
</tr>
<tr>
<td>Acid extraction + thermal integration</td>
<td>-20</td>
<td>“</td>
<td>100 - 200</td>
</tr>
<tr>
<td>FeSO₄ stabilization</td>
<td>-10</td>
<td>no</td>
<td>65</td>
</tr>
<tr>
<td>CO₂ stabilization</td>
<td>-10-20</td>
<td>no</td>
<td>80</td>
</tr>
<tr>
<td>PO₄ stabilization</td>
<td>+10-20?</td>
<td>no?</td>
<td>25</td>
</tr>
<tr>
<td>Landfilling: underground</td>
<td>no</td>
<td>no</td>
<td>100-150 (DE)</td>
</tr>
<tr>
<td>Backfilling underground: recovery as filler</td>
<td>no</td>
<td>yes</td>
<td>100-125 (DE)</td>
</tr>
<tr>
<td>Landfilling: surface level (hazardous waste)</td>
<td>no</td>
<td>no</td>
<td>100-125?</td>
</tr>
<tr>
<td>Landfilling: surface level (non hazardous waste)</td>
<td>no</td>
<td>no</td>
<td>50 - 100</td>
</tr>
</tbody>
</table>

1 Change of weight: The indicated percentage change of weight concerns a change in dry matter weight for the treated product compared to the dry matter weight of the original residue. Thus, one should observe that the true weight of treated residues could be higher due to an inherent content of water. Further, one should notice that some processes generate waste water with a possible content of dry matter (salts) originated from the virgin residue.
4. Recovery:

**Salts and gypsum**

It is possible to recover e.g. salts (NaCl, CaCl\(_2\), HCl) and gypsum by evaporation or crystallisation of the salt containing waste water from the flue gas cleaning wet system. The main objective of this operation is to avoid discharge of saline waste water to the sewage system.

The salt products are most commonly used in areas with de-icing demand in the winter time, or as regeneration salt in ion exchange systems in water softening plants. The main positive point seems to be, that a residual product like salt (or bine??) can substitute an otherwise purposely produced product and therefore reduces the overall energy consumed.

The costs for evaporation and storage for the recovered products are several times the costs for production of the same salts from natural resources.

If reuse of gypsum is not possible it has to be disposed off with a corresponding disposal cost.

**Salt mines**

Underground storage or landfilling is usually done by placing the residues only in salt mines; these may be old or in operation. The main purpose for this is typically either to avoid collapse of abandoned mine shafts and cavities, or to reinforce mine shafts in operating mines.

In Germany it is possible to dispose off waste underground for simple disposal as well as for reuse; however, this is only allowed in salt mines (Kavernen). The reason for this is justified in the fact that no free water exists in salt mines and that these are not in contact with ground water reservoirs.

More than 600 000 Mg/year of APC residues not only from Germany are recovered/landfilled that way.

Disposal of waste in coal mines (Bergwerken) is not allowed because substantial amounts of infiltration water is present and that this water could come into contact with ground water.

**Old limestone quarry**

APC is at the moment processed and landfilled in an old limestone quarry located on an island called Langøya, Norway. The residues are utilized in neutralisation of iron-containing H\(_2\)SO\(_4\); a waste product from Norwegian titanium industry.

Excess lime and buffer capacity in the APC residues are utilized in the neutralization process, and a part of the available heavy metals is precipitated mainly as metal hydroxides as well as incorporated in the gypsum. This probably results in some level of heavy metal retention; however it is not likely that this type of processing - in a long-term perspective - does significantly reduce leaching.

The deposit is not hydraulically connected to the surrounding sea but excess water from the deposit is treated to remove heavy metals and discharged to the sea. This is likely to continue while the facilities are in operation, however when the area is reclaimed the long-term leaching is determined by the contact with infiltrating water.
5. Treatment

**Solidification**

The main advantage of cement solidification is the reduced contact between water and residue and to some extent possible formation of less soluble metal hydroxides or carbonates. The solidified product is relatively easy to handle, and the risk of dusting is very low. The release of heavy metals from the products in a short-term perspective is typically relatively low, however the high pH of cement-based systems can result in significant leaching of amphoteric metals (Pb and Zn).

The drawbacks of this method are that leaching of soluble salts is not hampered and that this will eventually result in physical disintegration of the solidified product, thus allowing further leaching.

The addition of cement and additives increases the amount of waste to be handled; typically about 50 % of the residue dry weight is added as cement and additives and 30 to 100 % of the total dry weight is added as water (IAWG, 1997). Thus, the residue output from fly ash is typically increased from 20-30 kg/ton waste input to about 40-60 kg/ton waste, including addition of water corresponding to 50 % of the total dry weight.

**Thermal Treatment**

Thermal treatment of incineration residues is used extensively in a few countries mainly to reduce volume of the residues as well as to improve their leaching properties. Thermal treatment can be grouped into three categories: vitrification, melting and sintering. The differences between these processes are chiefly related to the characteristics and properties of the final product.

The techniques employed for vitrification and melting, or fusion of residues are similar in many respects. The main difference is the addition of glass forming additives in the case of vitrification. Several techniques for heating the residues are used: electrical melting systems (electric and plasma arc, resistance heating), fuel fired burner systems and blast melting. These differ only in the way the energy is transferred to the residues. Generally techniques are inspired from furnaces used in iron and steel production. In all systems, the residues are fed into a reaction chamber usually by a charger system. The melting process can be operated in such a way that a continuous cooler layer at the top of the smelter is maintained in order to confine the melting process, or the entire residue amount in the reaction chamber can be in a molten state.

Depending of the melting system, metal alloys can be recovered from the reaction chamber. Depending on temperatures in the reaction chamber and the state of oxidation or reduction of the gas phase, heavy metals (especially Cd and Pb) will be volatilized and removed by the off gas. All process configurations need off gas treatment systems to minimize emissions. In some cases they are combined with the off gas treatment of the MSWI plant.

**Extraction and separation**

Treatment options using extraction and separation processes can in principle include all types of processes extracting specific components from the residues. However, most emphasis has been put on processes involving extraction of heavy metals and salts with acid. Several techniques have been proposed both in Europe and in Japan. Most of these techniques make use of the acidic solution.
from the first scrubber in wet APC systems. The process is removing a significant part of the total amount of heavy metals from the residues (Cd: ≥ 85%; Zn: ≥ 85% ; Pb, Cu: ≥ 33% ; Hg: ≥ 95%) ; the leachability of the residue is reduced by a factor $10^2 – 10^3$. Zinc, Cadmium and Mercury are recycled.

**Chemical stabilisation**

The main concept of chemical stabilization is to bind the heavy metals in more insoluble forms than they are present in the original untreated residues. These stabilization methods make use of both precipitation of metals in new minerals as well as binding of metals to minerals by sorption. These processes include some sort of solubilization of the heavy metals in the residues and a subsequent precipitation in or sorption to new minerals. Several of the stabilization methods have an initial washing step where a major part of soluble salts and to some extent metals are extracted before chemical binding of the remaining metals. These methods are finalized by dewatering the stabilized product, which is then ready for landfilling.

The main advantage of Ferrox stabilization is improved leaching properties of the final product. The leaching characteristics of treated residues are shown to be very good (Lundtorp, 2001), and it is expected that low release of heavy metals can be maintained for extended periods of time, as iron oxides are known to endure in geological time frames. The pollution potential of the treated residues is documented rather detailed and the treated residues are expected to be less prone to physical disintegration than cement stabilized products because of the fact that most salts are removed. Ferrox stabilized residues typically have far better leaching properties than cement solidified residues.

The CO$_2$ stabilization VKI (new technology) stabilization resembles in many respects the Ferrox stabilization process, however the chemical agents used here are CO$_2$ and/or H$_3$PO$_4$. The VKI-process involves a two-step procedure where the residues are first washed at L/S 3 l/kg in order to extract soluble salts. After this the residues are dewatered and washed again in a plate and frame filter press at L/S 3 l/kg. The residues are then re-suspended, and CO$_2$ and/or H$_3$PO$_4$ is added. The stabilization reactions are allowed to occur for 1-1.5 hours while pH decreases, and another hour where pH is maintained around pH 7. Finally, the residues are dewatered again and washed at the filter press with another 3 l/kg. The final product has a water content of about 50 %. The use of CO$_2$ and H$_3$PO$_4$ as stabilizing agent ensures that heavy metals are bound as carbonates or phosphates.

VKI stabilization shows very good leaching properties similar to the Ferrox stabilization. Metal carbonates and phosphates are known to generally have low solubilities, and the leaching characteristics of VKI stabilized residues are expected to remain good for extended periods of time. The pollution potential of the treated residues is documented rather detailed and physical disintegration of the treated residues in a long-term perspective is expected to be less important than in the case of cement stabilization, because of the fact that most salts are removed. VKI stabilized residues typically have far better leaching properties than cement solidified residues.

The VKI process reduces the amount of residue by about 15 % per dry weight.

PO$_4$ stabilization (WES-PHix®) (new technology) is a chemical stabilization with phosphate as the stabilization agent is used in the WES-PHix stabilization process. The treatment process is
relatively simple, and consists of a mixing device (such as a pug mill) into which the residues are fed at a controlled rate. A proprietary form of soluble phosphate is then added to the mixer. After the phosphate is thoroughly mixed with the residues, a conveyor at the end of the mixer then removes the treated product. In some cases, depending on the characteristics of the residue input, other additives such as lime are used. Reaction kinetics are fast and the residue is considered fully treated without further curing (Wheelabrator, 2002).

The process retains salts in the treated product, thus facilitating a substantial leaching of these and increased solubility of some heavy metals (e.g. Pb and Cd) after landfilling. Compared to the Ferrox and VKI processes relatively small amounts of water are added along with the phosphate. The release of salt and heavy metals is expected to be higher than is the case with Ferrox and VKI treated residues.

6. Conclusion

Although many ways of both recovery and treatment methods for APC residues are well known landfilling is still the predominating option – in many parts of the world due to the lack of economic regulatory incentives.

Landfill design and operation can potentially diminish or enhance contaminant release from the APC residues. Any type of landfilling should include an assessment of the environmental impact both in the short- and long-term perspective, and should be a part of a proper disposal strategy that takes the treatment into account. However, it is evident that the design should assist in minimizing the total lifetime of required active environmental protection systems. The following should be considered:

- The properties of the waste,
- the potential risks related to handling and landfilling,
- the long-term effects of keeping the residues at the disposal site
- consequence of operating the landfill (for example, effects of leachate management).

At the termination of the active care period, emissions from the residues remaining must be at an environmentally acceptable level without the need of any active operation.

With respect to APC residues, the main objective of landfilling is to remove the residues from general circulation and to ensure that the release of contaminants from the residues occurs at acceptable levels and preferably at levels similar to natural geological materials. To fulfil this requirement, most cases involve some level of residue treatment before placing the residues at the landfill. In many European countries the aim is to ensure that leachate from landfilled waste is acceptable in the surrounding environment without the need of treatment after an active phase of about 30-50 years. By their nature, APC residues can potentially leach out high concentrations of heavy metals for very long time frames and cannot meet this requirement without either substantial treatment before or under landfilling favourable hydraulic conditions.

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