Goumans/Senden/van der Sloot, Editors
Waste Materials in Construction: Putting Theory into Practice

Pre-treatment of MSWI fly ash for useful application

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Abstract

At TNO a feasibility study has been carried out into the possibilities of removing a number of easily leachable elements from MSWI fly ash. The aim of this study was to find a way to usefully apply MSWI fly ash (after treatment) as a road base construction material. A combination of a slight washing step and a stabilisation/solidification-step with cement and other additives appeared to be convenient to meet the severe standards of the Dutch Building Materials Decree.
The slight washing step removes the cadmium and chloride that originally was present for more than 90%. Zinc and sulphate are removed for more than 50%. The remaining solid material (approximately 70% of the original quantity) can be easily processed into a bound road foundation layer, adding some 20% cement and other additives. The leaching characteristics of the stabilised material meet the most severe standards of the Dutch Building Materials Decree in the Netherlands. This means, that the material may be applied without any provisions. To the contrary, stabilised MSWI fly ash (that was not washed) could not even meet the less severe standards.
Some preliminary experiments with a Pilot Plant Installation show promising results. Chloride in particular can be removed to the same extent as was found in the batch experiment. The removal of some metals seem to be more complicated. This is subject for further research.
A global cost estimate shows that, for the Dutch situation anyway, the processing costs of the combination (washing, processing of the washing liquor, and stabilisation) equals the costs for disposal of MSWI fly ash.

1. Introduction

In the Netherlands the fly ash from Municipal Solid Waste Incinerators (MSWI) is considered hazardous waste. The Building Materials Decree (BMD) nevertheless allows the useful application of such wastes. Therefore the waste should meet de standards for leaching set in the Decree.
Several studies have been performed to develop processes for making applications with MSWI fly ash. In those processes the fly ash was stabilised or solidified with for instance cement. All these attempts have been unsuccessful so far due to high leaching

values for anions in particular. Together with metals like cadmium, molybdenum and zinc, anions tend to be easy leachable.

Other processes are based on thermal treatment of the MSWI fly ash. Most of these processes achieve sufficiently stabilisation/solidification of the metals, but not for the anions.

For this reason TNO tried to pre-treat the MSWI fly ash before stabilisation or solidification. For this purpose the possibilities of a slight washing step were studied. The aim was to develop a technique with which MSWI fly ash is transformed into a secondary building material. The washing should be sufficient to remove the easy leachable components.

This aim is in contrast with for instance the 3R-process, where it is the intention to leach as much of the heavy metals as possible [1]. In the 3R-process the removal of the metals is the main goal, whereas in the TNO development the production of a secondary raw material is the main goal.

2. Washing of MSWI fly ash (batch experiment)

A batch experiment was carried out on some forty kilograms of MSWI fly ash. The fly ash was mixed with water in a liquid solid ratio of 10 l/kg. Under intensive stirring the pH was maintained at 4 by adding nitric acid during the experiment. The acid consumption was some 3 mole acid per kg fly ash. This is a little less than the amount Laethem e.a. needed in their experiments [3]. After 4 hours the mixture was filtered over a paper filter. The cake was subsequently washed twice with fresh water in a lower L/S ratio of about 2.

After the experiment the cake was dried and analysed right after filtration. The moisture content of the cake was approximately 30%. During the experiment some 30% of the fly ash was dissolved. Also the wash-water was analysed. The results of the experiment are presented in Table 1.

Table 1: Results of the washing experiment

Elements	Original concen-trations (mg/kg)	Concentrations after washing (mg/kg)[1)]	Decrease in concentration[2)]
Cd	220	32	90 %
Cu	660	920	3 %
Mo	17	23	5 %
Pb	6000	7800	9 %
Zn	14000	6900	66 %
Cl^-	53000	5800	92 %
SO_4^{2-}	64000	79000	14 %

1) = Measured in the solid mass after washing and drying

2) = After correction for mass reduction of about 30%

The conclusions of this washing experiment are:

1. The acid consumption of washing MSWI fly ash at a constant pH of 4 is approximately 3 mole acid per kg fly ash.
2. A reduction in weight of about 30% occurs, mainly caused by the dissolving of the salts.
3. Most of the cadmium, chloride and zinc are removed.
4. Sulphate is also removed, although to a lesser extent,.
5. Copper, lead and molybdenum are not substantially removed.

3. Useful application of the washed fly ash

The washed fly ash from the batch experiment was stabilised with cement. The stabilisation was conducted at a road construction firm, specialised in applying waste materials as secondary raw material. The application aimed at was a road base foundation layer. The stabilisation was performed on the washed fly ash as well as on the unwashed fly ash.

Of both types of fly ash proctor cylinders were made. In total some 20% of additives were needed to make proper cylinders with the fly ash. The additives comprised mostly of cement, stabilising additives and water.

Both types of proctor cylinders hardened well. The cylinder made with washed fly ash had a low porosity in particular. This was proven by the results of the diffusion test. One of these results is the tortuosity factor, which stands for the porosity of the tested material. A high tortuosity factor means that the porosity is low. The tortuosity of the proctor cylinder made with washed fly ash was 20,000, whereas the tortuosity of the proctor cylinder made with unwashed fly ash was 320. The tortuosity of normal concrete is approximately 1,000.

The proctor cylinders were tested with the diffusion test (or tank leaching test) according to the Dutch standard NEN 7345. In this test the intact (solidified) product is immersed in acidified, demineralised water. The water is renewed at seven times, up to 64 days. Afterwards the eluates are analysed and diffusion coefficients are calculated from the results. Also emissions are calculated, expressed in mg/m^2.

Table 2: Results of diffusion leaching tests after stabilisation/solidification:

Element	Stabilisation/solidification product of **un**washed fly ash (mg/m^2)	Stabilisation/solidification product of washed fly ash (mg/m^2)	Standards for Category **1** applications
Cu	7	7	51
Mo	**48**	4	14
Pb	64	61	120
Zn	88	14	200
Cl^-	**420000**	680	18000

Table 2 presents the emissions form both the cylinders as well as the standards according BMD. The standards presented are meant for category 1 materials. Category 1 materials may be applied without any restrictions. This means that these standards are the most severe. On the other hand, category 2 material may be applied only if provisions are taken that prohibit or prevent leaching.

Table 2 presents clearly that washing of MSWI fly ash decreases the leaching of chloride, zinc and molybdenum. The decrease in leachability of zinc and chloride can be explained from the results of the washing step; the greater part of the zinc and chloride, present in the original fly ash, were washed out.
The decrease of the leachability of molybdenum cannot be explained from the results of the washing experiment. Molybdenum was washed out for only 5%. Most probably the serious leaching of molybdenum from the unwashed material is caused by the increasing porosity of the material during the leaching test. During the leaching test 24,000 mg/kg chloride is leached; more than half of the quantity, available for leaching. This causes the formation of a reasonably porous structure during the performance of the test. The different fractions of the leaching test indeed show increasing molybdenum concentrations, with the course of the test. Also the difference in tortuosity points into that direction (as is mentioned before).
From the comparison of the emissions with the standards of the Building Materials Decree (BMD) it can concluded that the washed and stabilised fly ash may be applied as category 1 building material. The stabilised unwashed fly ash, on the other hand, may not even be applied as category 2 building material due to high emissions of chloride and molybdenum.

4. Pilot plant

Consequently TNO developed a Pilot Plant Installation for treating MSWI fly ash with a slight washing step. The installation comprises a three counter current washing units. Figure 1 shows the TNO Pilot Plant for washing granular materials.

With this installation experiments of different conditions for slightly washing fly ash are currently being performed.
Preliminary experiments with this installation show that the results of the batch experiment can be reproduced for the anions at even lower liquid/solid ratios and higher pH. This means a significant reduction in the use of both fresh water and acid. Chloride in particular was removed to a large extent. However the metals cannot be removed as good as was found in the batch experiments. Possibly due to big differences in pH values in the successive washing steps the metals are partly precipitated again. This is subject to further research at the moment.
Furthermore running a counter current process is proven feasible. Results of experiments performed with this installation are not yet available.

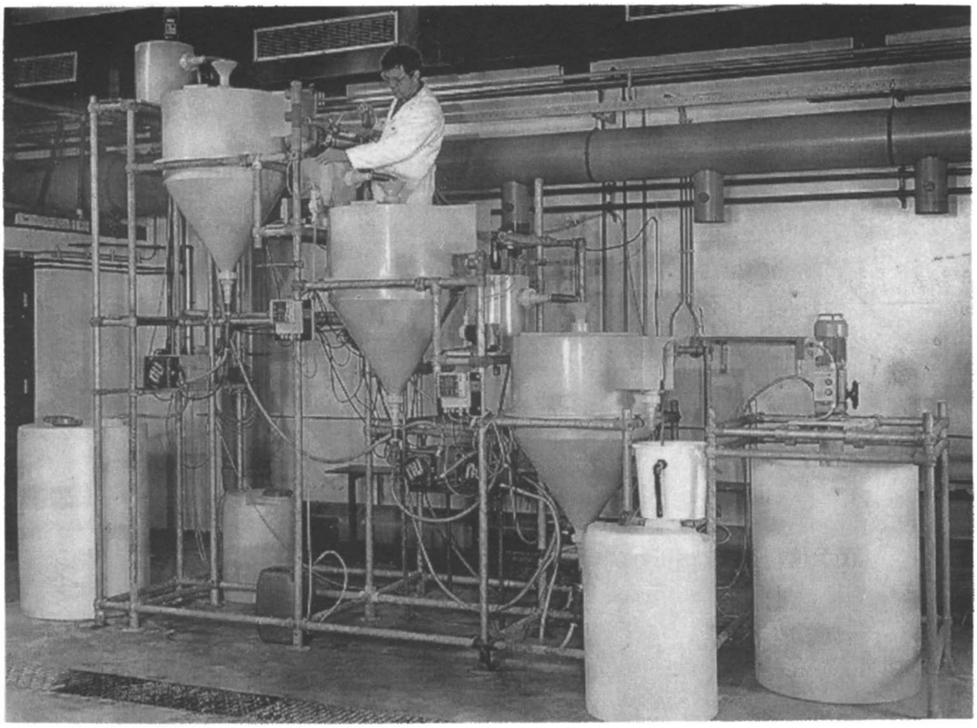

Figure 1: Pilot plant for continuous washing of fly-ash.

The most feasible application of a slight washing process at a municipal waste incinerator (MSWI), is to integrate it in the scrubbing system of the incinerator. For the scrubbing of MSWI flue gases, in the Netherlands most of the time a wet process is used comprising of two steps and produces a waste water stream. This stream is neutralised, precipitated and filtered to remove the heavy metals as a hydroxide sludge. The remaining salt water is either drained away or evaporated.
As is shown in figure 1, the washing process yields a waste water stream as well. This stream can be fed into the waste water treatment process of the incinerator. Part of the filtrate may be recycled in the washing process to increase the metal concentration. In particular a high zinc concentration could make recovery of this metal economical feasible.

5. Process Costs

The costs of the washing process, taking into account the extra costs of waste water treatment and a negative price of the washed fly ash, and based on an installed capacity of 10,000 tons/year, is roughly estimated at Dfl 200,-. These relatively high costs consist mainly of acid used, waste water treatment costs, disposal costs of the waste water treatment filter cake and a negative price of the washed fly ash of Dfl 50,- per ton.

The total costs of Dfl 200,- per ton fly ash is lower than the current disposal costs of MSWI fly ash as a hazardous waste. However, in The Netherlands disposal of untreated MSWI fly ash will be prohibited in the near future. In that situation Dfl 200,- per ton is considerably lower than that of stabilization/solidification, followed by disposal as a 'less' hazardous waste or of vitrification, followed by useful application of the product.
The process costs may be lowered by using acid from the first flue gas scrubbing step as leaching acid or by using less acid. Also the disposal costs of the filter cake may be reduced, by means of stabilization/solidification, followed by disposal as a 'less' hazardous waste.

6. Conclusions

The following conclusions can be drawn from the results of the work that has been done:

1. A 'slight' washing step is a promising way of pre-treating MSWI fly ash before useful application. After washing the fly ash can be applied as for instance a secondary raw material in road construction. Even application in concrete seems to be possible.
2. Slight washing of fly ash removes easily leachable components as cadmium, zinc and chloride for 70 to 90%. The bulk of the fly ash remains as it was.
3. Useful application of the washed fly ash after stabilisation/solidification is environmentally acceptable. The leaching values of some key elements from a test proctor cylinder made with washed fly ash are below the limit values of the Dutch Building Materials Decree.
4. The most simple, and therefore most feasible way of implementing the slight washing process, is integrating the process in the scrubbing system of the incinerator.
5. The costs of the washing fly ash are estimated to be about the same or even lower than the current disposal costs of fly ash. Of more importance is the fact that after washing the fly ash can be usefully applied.
6. A counter current washing process of fly ash has proven to be technically feasible on pilot scale.

References

[1] J. Vehlow, e.a., Semi Technical demonstration of the 3R-process, Waste Management & Research No. 8 (1990), 461 - 472.

[2] R.K. Zijlstra and E. Mulder, Feasibility study of washing and useful application of MSWI fly ashes, TNO-report, Apeldoorn, september 1994, (in Dutch).

[3] B. Laethem, e.a., Integrated treatment of MSWI-residues; treatment of fly ash in view of metal recovery, Studies in Environmental Science 60, Environmental aspects of construction with waste materials, Elsevier (1994), 525 - 537.