

Improvement of Environmental Quality of Coal Fly Ash by Applying Forced Leaching

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ABSTRACT

A coal fly ash containing leachable trace elements in amounts higher than allowed by Dutch law for its free application as granular building material was subjected to forced leaching using water, citrate-, oxalate-, EDTA- and carbonate-solutions. With water only, the free lime and substantial amounts of Mo (30%), Se (20-40%) and SO_4^{2-} (40-50%) are removed. Using the extraction agents, these percentages increase to 60-90% and in addition 15-20% Cr, V and Sb are removed. The environmental quality of the washed fly ash was checked with the Dutch standard leaching test (NEN7343). Leachability of Mo, Se and S decreased by a factor of 2-4 after washing with water and a factor 2-18 (including Cr) after washing with the extracting agents. Although leaching values for individual elements complying with Dutch standards have been achieved, none of the conditions proved to produce a residue fully compliant with the law. Improvements by removing components remaining in the moisture after filtration are required. For a feasible process further reduction of reagent consumption and simple methods for processwater recycling are needed.

INTRODUCTION

The total coal fly ash production of 800,000 t/yr in the Netherlands including technically less suitable portions is reused in so-called “bound” applications, mainly in cement and concrete products. Landfilling has become expensive and environmental laws exclude the use of coal fly ash in “unbound” applications as granular building materials. The prevailing Decree on Building Materials (BsB) prescribes a standardized leaching test for granular building materials. The leaching limits stated in this decree are based on the principle that through leaching from building materials the increase in concentration of any compound in the underlying soil should not be higher than 1% relative to a standard soil over 100 years calculated over the first 1m in depth in that soil. Thus, numerical values depend on the thickness of the application used and the effective infiltration into the soil. Two categories are distinguished. Category 1 assumes 300mm/yr of effective infiltration, compatible with the average yearly rainfall in the Netherlands. Category 2 allows only 6mm/yr of effective infiltration that can only be obtained when protective measures are taken. In this paper the numerical values for comparison are taken for Category 1 Building Materials applied at a height of 1m. Surveys done by RIVM² and KEMA³ on leaching of coal fly ashes produced in the Netherlands are summarized in Table 1. These data show that leaching of Mo is above the norms of the BsB in all analyzed ashes and that for Se, Sb, Cr, V and SO_4 this is also very often the case. To the

contrary it must be noted that elements often considered suspicious, such as As, Cd and Pb, do not normally show leaching values above the norms.

The aim of the present study is the removal of that portion of the elements that contributes to leaching without changing the physical properties of the ash and without extracting major elements. The washed residue should show improved leaching characteristics, if possible complying with the norms of the BsB.

Table 1 Leaching behavior of Dutch coal fly ashes, determined according to the standard leaching test NEN7343¹ (L/S=10), expressed in mg/kg.

	RIVM/RIZA, 1993 ²				KEMA, 1995 ³				BsB Cat 1 h=1m
	Average	Min	Max	n	Average	Max	Min	n	
As	0.263	0.022	0.987	12	0.07	0.014	0.28	26	0.87
Ba	2.166	0.032	3.200	5	6.1	1.3	22.8	26	4.2
Cd	0.004	0.000	0.011	17	0.0008	0.0004	0.0040	26	0.029
Co	0.018	0.010	0.025	2	0.012	0.006	0.060	26	0.35
Cr	1.729	0.160	4.673	17	1.3	0.2	3.6	26	0.92
Cu	0.080	0.007	0.685	7	0.015	0.009	0.050	26	0.58
Mo	5.81	0.350	15.260	16	5.9	1.3	10.3	26	0.24
Ni	0.064	0.010	0.676	10	0.03	0.01	0.36	26	0.95
Pb	0.051	0.004	0.109	9	0.22	0.02	3.80	25	1.6
Sb	0.203	0.004	0.370	5	0.059	0.010	0.191	26	0.039
Se	1.335	0.010	3.700	6	0.96	0.04	4.80	26	0.039
V	3.969	0.350	17.490	9	1.7	0.1	9.9	26	1.4
Zn	0.213	0.065	1.017	5	0.068	0.033	0.300	26	3.3
SO ₄ ²⁻	3088	1342	3842	6	1529	85	5160	26	1122

MATERIALS AND METHODS

Fly ash used

An alkaline coal fly ash was sampled from a representative electric power plant in the Netherlands burning a blend of imported coals. The composition of this ash is given in Table 2.

Table 2 Chemical composition of the used fly ash

Major elements (%)				Trace elements (mg/kg)			
SiO ₂	46.9	K ₂ O	2.1	As	27.7	Ni	138
TiO ₂	0.2	Na ₂ O	1.2	B	308	Pb	126
Al ₂ O ₃	24.9	P ₂ O ₅	0.7	Ba	2166	Sb	16.1
Fe ₂ O ₃	8.8	SO ₃	1.0	Co	66.1	Se	16.1
MnO	0.1	LOI	1.6	Cr	154	V	320
MgO	3.8			Cu	214	Zn	217
CaO	6.9			Mo	11.2		

Extraction tests

Extraction tests have been carried out using 50g samples of the above-mentioned fly ash. The samples were added to the appropriate amount of solution in a beakerglass while stirring to keep all solids in suspension. After the predetermined time, the suspension was quickly filtered on a 0.45µm membrane filter in order to obtain enough solution for analysis. The solutions were

analyzed by ICP and AAS for the most critical heavy metals and some major elements. The variables used were the nature of the extracting solution, the concentration of the extractant, the L/S ratio (from 1 to 50) and the reaction time (from 5 minutes to 4 hours). The extracting solutions and range of concentrations used are:

- Water (both distilled and tap water)
- H₄EDTA: 0.01-0.1 M.
- Oxalate buffer consisting of a mixture of ammoniumoxalate and oxalic acid in a ratio of 1.75, ranging from oxalic acid concentrations of 0.025 to 0.2 M.
- Citrate buffer consisting of a mixture of ammoniumcitrate and citric acid in a ratio of 1.75, ranging from citric acid concentrations of 0.025 to 0.15 M.
- Ammoniumcarbonate: 0.05 – 0.4 M.

Washing tests

For the optimum conditions of extraction, a number of tests were repeated with samples of 1kg each, in order to obtain sufficient residue to perform leaching tests. Now samples were completely filtered after extraction (L/S=5 except for ammonium carbonate for which L/S=2 was used), which took some time during which the remaining solution was still in contact with the solid settled on the filter, resulting in less precisely determined reaction times. The moisture content of the residue after filtration was found to be about 25%. The filtercake was again suspended in clean water at an L/S ratio of 2 and stirred for 10 minutes before second filtration. To wash away extraction agents further, clean water was poured on the filter in two portions equivalent to L/S=2 each. Samples from the four solutions were taken and analyzed so that total removal of heavy metals and the portion left behind in the moisture could be calculated.

Leaching tests

This test, NEN7343¹, consists of slow upflow percolation (maximum 25ml/kg.hr) of preconditioned water (pH=4) through a 5cm diameter column filled with the material over a length of at least 20cm until a final liquid/ratio of 10 is reached. In total this test will last about three weeks. Samples of the percolate are taken at determined intervals and the analyses give an idea of the history of the leaching. The calculated concentrations of the composite sample are to be compared with the norms in the BsB.

RESULTS AND DISCUSSION

Extraction tests

With water, only SO₄²⁻ (±40%), Mo (±30%) and Se (20-30%) is removed in a counter-current washing system with an effective L/S=9. The only other detectable element in solution is Ca (±15% removed) from the dissolution of the free lime and CaSO₄. This gives the solution a pH of about 12-12.5. The solution can be cleaned by bubbling CO₂ through it forcing precipitation of CaCO₃ accompanied by coprecipitation of Se(IV)⁴. Precipitation of ettringite to remove sulphate is under investigation. Mo can be cleaned using anion exchange resins.

Using extraction agents higher amounts of these elements were extracted, but in addition also considerable amounts of Sb, Cr, V, As, Zn, Ni and other heavy metals. For most extraction agents a certain concentration was required to achieve reasonable extraction efficiency.

Increasing the concentration generally results in an increase of extraction of heavy metals, but often also in an even stronger increase of extraction of the major elements Ca, Al and/or Si. Figure 1 illustrates this for the citrate buffer at constant L/S=5 and reaction time of 1 hour.

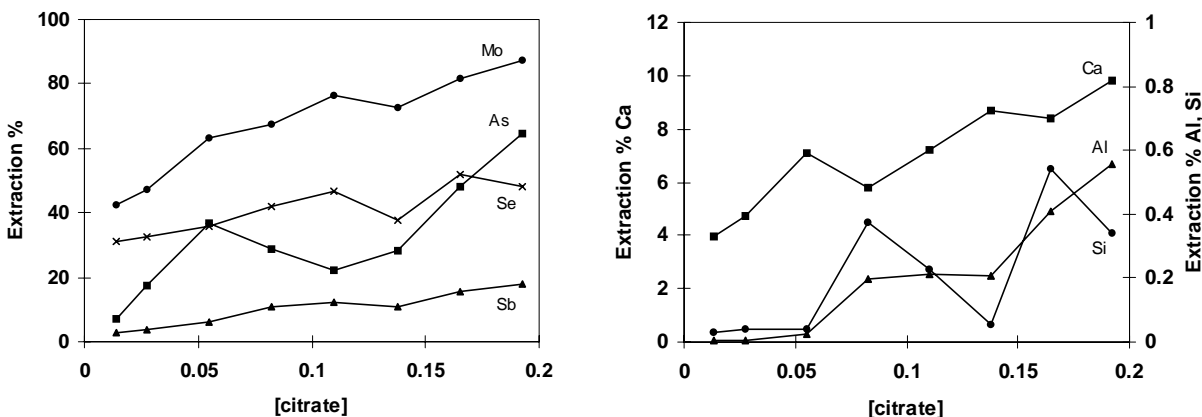


Fig.1. Extraction of trace and major elements with the citrate buffer at L/S=5 and t=1hr.

By varying the L/S ratios at constant concentrations and reaction times it was found that for extraction of trace elements L/S=5 was the most appropriate, except for ammonium carbonate for which L/S=2 seems to be sufficient. Increasing L/S further only resulted in higher extraction of major elements, however without improvement of the extraction for trace elements.

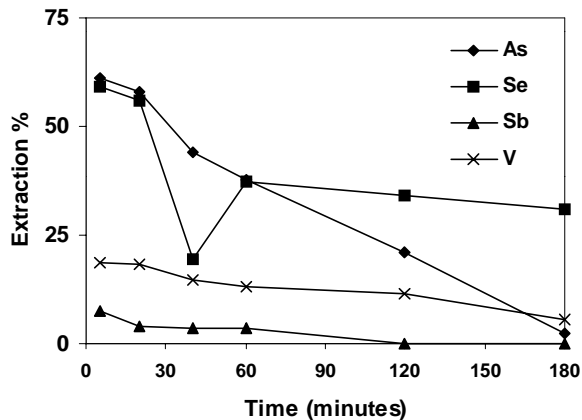


Fig. 2. Decrease of extraction of As, Se, Sb and V with time due to reprecipitation; 0.05 M H₄EDTA, L/S=5.

Complexation reactions are generally fast and reaction times of 5 to 15 minutes have proved to be long enough to obtain maximum extraction for most heavy metals. Because extraction of Ca and at a later stage Mg continues, the pH of the solutions slowly increases with prolonged extraction, which may result in reprecipitation of certain elements that were already extracted at an early stage. This effect is illustrated in figure 2 for extraction of As, Se, Sb and V with EDTA. It also occurs in some cases for Cr and the major elements Si and Al. Such reprecipitations must be avoided since the precipitated phases may be soluble under different conditions, which may cause enhanced leaching during the column tests. Modeling the solutions with MINTEQA2 revealed that Cr₂O₃, Cr(OH)₃, MgCr₂O₄, V₂O₄ and VO(OH)₂ are possible phases responsible for the decrease of Cr and V in these solutions. For Se and Sb no such phases were found, and for As the decrease is possibly due to coprecipitation with Fe-oxides or -hydroxides.

It was found that 60-90% of the SO₄²⁻, Mo and Se and 15-20% of Cr, Sb and V could be extracted under the best conditions with the reagents used (see also table 3).

Washing tests

The results of the removal of the environmentally most critical elements obtained under favorable conditions during the tests with 1 kg samples is given in table 3. In this calculation has been taken into account the amounts removed during the post-extraction washing with water and the amounts left behind in the moisture of the residues. Because Ca forms stable complexes with most reagents used, a combination of washing with water and extraction agents is proposed, thus eliminating a large portion of the readily available Ca before the complexing reagents are used. Preliminary results show that higher total extractions can be obtained and that similar extractions are possible with lower reagent consumption.

Table 3 Removal of trace elements from fly ash with 1 kg samples under selected conditions. Except for water, procedures have been followed as described under Material and Methods.

	Water: 4-step counter current Eff. L/S=9	H ₄ EDTA 0.05 M t=20 min.	H ₄ EDTA 0.05 M t=10 min.	Oxalate buffer 0.105M/0.06M t=120 min.	Citrate buffer 0.105M/0.06M t=60 min.	Amm.carbonate 0.25 M t=60 min.
Cr	----	9.3	12.1	10.9	19.0	16.4
Mo	27.1	78.6	77.7	63.7	91.4	85.8
Sb	----	5.9	8.9	20.3	21.4	7.6
Se	18.5	38.4	62.0	72.5	46.8	35.9
SO ₄ ²⁻	37.9	65.2	69.8	80.2	78.6	100.0
V	----	11.9	21.4	9.1	18.5	3.9

Column tests

The results of the standard leaching tests (NEN7343) carried out with the residues obtained from the washing tests described above are given in table 4. Washing with water improved the environmental quality of the fly ash as far as the removed elements Mo, Se and SO₄²⁻ are concerned, but not sufficiently to comply with the norms. Washing with extraction agents had the effect of decreasing the leaching, but only in few cases enough to comply with the norms for Cr, Mo and SO₄²⁻. Se, although improved, never got under the norm, which is mainly due to the very low requirements imposed (0.039 mg/kg).

Table 4 Leaching (mg/kg) according to standard column test NEN7343 of residues obtained from washing of fly ash according to table 3. Bold figures are above the norms of the Dutch Building Decree for Category 1 building materials at application height of 1m

	Norm BD C1, 1m	Untreated ash	Water washed	H ₄ EDTA 20 min.	H ₄ EDTA 10 min.	Oxalate buffer	Citrate buffer	Amm. carbonate
Cr	0.92	4.31	4.79	0.48	0.90	1.04	1.33	0.34
Mo	0.24	4.00	1.38	0.19	0.42	0.54	0.41	0.19
Sb	0.039	0.018	0.040	0.050	0.020	0.080	0.210	0.150
Se	0.039	0.473	0.260	0.190	0.140	0.650	0.170	0.370
SO ₄ ²⁻	1122	5536	2301	1044	1296	1152	1155	390
V	1.40	<0.05	0.24	0.45	0.51	0.74	0.52	0.80

In this respect the metals present in the moisture adhering to the residues after the last filtration step are important since they must be considered as highly mobile and will therefore be released during the initial stage of leaching. Assuming 20-25% moisture in the residue, analyses of the last filtrate indicate that for Se, Mo and Cr between 0.06 and 0.1 mg/kg remains present in this mobile form, which is already above the norm for Se. Moreover, remnants of extracting agents

may also cause further release of metals during the leaching test. So, in order to obtain results complying with the norms of the BsB, total removal of mobile metals and extractant residues from the washed fly ash is required. A possible way might be the sequestering by coarse and easy removable pellets of a strong adsorbent (clay or zeolite), applied during the post-extraction washing step.

For Sb and V the leaching has increased by the washing, giving often leaching values above norms for Sb. This is possibly due to the effect of quick release followed by reprecipitation as discussed above.

CONCLUSIONS

The present study shows that it is possible to remove a high percentage of trace elements from fly ash and that this results in improvement of the leaching behavior of the residues. However, compliance with Dutch leaching requirements for building materials could not yet been obtained. Improvements may be anticipated if the remainder of extracting agents and mobile metals can be removed efficiently from the moisture left behind in the residues after filtration. Further improvements are possible when washing with water is done as a pretreatment before extraction with reagents.

However, in order to obtain a feasible process further reduction of reagent consumption must be achieved by regenerating and recirculating of the majority of the processwater. Simple methods for decontaminating the solutions must be developed as well as clear outlets for the resulting concentrated wastes to be determined.

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