

Potential Element Retention by Weathered Pulverised Fuel Ash : I. Batch Leaching Experiments

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ABSTRACT: Three PFA (Pulverised Fuel Ash) samples, which were fresh, 17 and some 40 years weathered, were collected from two major British power plants. Batch leaching tests with these samples using distilled water and simulated industrial leachate showed higher amounts of element liberation from fresh ash, including Ca, Na, K, S (as SO_4^{2-}), Cr_{total} , Cu, Li, Ni, Mo and Cl^- and this seems to indicate their surface association and easier dissolution when contact with water. On the contrary Mg, Al, Ba, Si, V, As and Se do not show such readily leachable concentrations and these elements might be more associated with glass fraction in PFA particle rather than surface. Although element concentrations in the weathered ash are much lower than those in the initial leachate from the fresh ash, elements are still detected at reasonable concentrations, with rather constant levels and this seems to demonstrate the element release from unstable glass phase of PFA particle. Fe, Ca, Cr_{total} , Cu, Ni, Zn and Hg were removed from the synthetic leachate by PFA and this is also confirmed by gain in solid PFA. The order of element retention is Meaford weathered ash > Drax weathered ash > Drax fresh ash in decreasing order and this conforms with the degree of weathering. Namely, the more weathered, the more effective in metal retention from the synthetic leachate.

INTRODUCTION

The mineral matter present in coals is a major contributor to the composition of the pulverised fuel ash (PFA) produced in a coal-fired power station. Elements are concentrated in the ash compared with the coal because of the loss of carbon on ignition. For those elements mainly associated with the detrital minerals concentrations in the coal ash are comparable with adjacent shales and mudstones. Other elements, however, are associated either with minerals formed in the coal or in the organic matter itself. These latter elements may be concentrated in PFA and be present at much higher levels than in most geological materials. Another problem is that most geological materials react slowly, if at all, under low temperature weathering conditions, whereas PFA contains soluble sublimates in addition to the unstable silicate glass.

The potential problem of leachates from PFA has been investigated in field and laboratory studies. Attention has mainly focused on those elements which are readily liberated into solution and lost from the ash (Eary *et al.*, 1990; Mattigod *et al.*, 1990). The longer-term weathering of the ash has received less attention was recently investigated (Lee, 1994; Lee and Spears, 1995). The rate of release of elements into solution may be sufficiently

slow that the environmental impact on surface waters is negligible because of dilution effects, but this need not apply to groundwaters. The weathering of PFA will also produce insoluble reaction products and the mobility of elements could be reduced by reaction with the secondary products. If such reactions are significant weathered PFA could provide some amelioration for leachates generated by other waste materials. In order to examine such a possibility experimental work was undertaken in the laboratory, using weathered PFA and simulated leachates. Two experimental procedures were adopted, one of batch leaching reported here, and the other of column leaching, which will be discussed in a separate paper. The procedures adopted differ to the standard leaching experiments in that a cocktail of metals in a simulated leachate was used in addition to distilled water, with the objective of determining the potential loss of elements from solution.

EXPERIMENTS

Samples

The weathered PFA samples used in this investigation were obtained from the Barlow disposal mound [National Grid Reference SE 655 277] at Drax Power Station and from the decommissioned power station at Meaford [NGR SJ 896 373].

The PFA is added to the mound at Barlow by lateral

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Table 1. Composition of the synthetic leachate used in the batch leaching test (analysis by ICP-AES, Unit: mg/l unless indicated). Those elements whose concentrations are shown in brackets originate as impurities in the standard chemicals.

pH	Ca	Na	K	Mg	Fe	Al	B	Ba	Cd
4.55	615	1032	735	87	123	(0.12)	(0.23)	0.04	121
Cr	Cu	Li	Mn	Ni	Pb	Si	Sr	Ti	V
80	118	19	(0.18)	109	0.22	(0.81)	(0.16)	(0.05)	(0.11)
Zn	As	Hg	Se	Mo	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻		
108	(0.27)	13.8	(0.33)	(0.68)	1973	21	419		

tipping to the full height of the mound. Soil is added and vegetation quickly established. It is known when the vegetation was planted and the age of the PFA can therefore be established. Samples were obtained from a shallow pit at depths of between 50 and 80 cm from surface in PFA emplaced in 1975. Fresh PFA was also collected from Drax in order to compare with the weathered PFA.

Meaford was selected for additional sampling in order to extend the age range of the material examined. At Meaford the PFA was initially pumped into lagoons and then transferred to a mound on a natural hillslope. The mound now forms a plateau which has been grassed over and returned to agricultural use. Ash samples were again obtained from a shallow pit located on the plateau at a depth of between 50 and 80cm. The PFA cannot be dated as accurately as at Barlow because ash disposal is not well documented. It is known, however, that the age of the ash is at least 20 years and is probably between 20 and 40 years.

Composition of Simulated Leachate

A solution was prepared similar in composition to that of leachate resulting from the co-disposal of domestic and industrial waste with the exception of the heavy metals, which are approximately ten times higher than normally encountered (Table 1). A synthetic leachate of similar composition was used in the work of Newman and Ross (1985). In addition to the elements present as major components other elements are present as trace impurities. These elements are also shown on Table 1. The leachate includes the following organic components, acetic acid (5000 mg/l), propionic acid (3000 mg/l), butyric acid (2000 mg/l) and phenol (20 mg/l) which were included to more closely simulate natural leachates but were not analysed in this work because the experiments were designed to examine metal uptake. Finally the synthetic leachate was adjusted to pH 4.5 with ammonia.

Batch Leaching-Experimental Procedure

The batch leaching was based on Standard Method DIN 38414-S4 (October, 1984), the German standard for the determination of the leachability of sludge and sediments by water.

50 gms of the three PFA samples (fresh Drax, weathered Drax, and weathered Meaford) were placed in 1 litre polypropylene bottles and 500 ml simulated leachate solution added to each. The bottles were then shaken for 24-hours in an end-over-end shaker and the eluate filtered through a 0.45 μ membrane filter under vacuum. The Eh, pH and electrical conductivity were measured and the solution acidified with 1% HNO₃. The procedure was repeated a further three times but with the simulated leachate replaced by distilled water.

The above procedure is to determine the loss of elements from solution and thus the gain onto the PFA, but there will also be some elements which are leached from the PFA. This contribution to solution was determined on the three samples using distilled water instead of the leachate solution followed by further additions of distilled water, as in the above procedure.

Cations were determined using ICP-AES. A second ICP laboratory was used to check the quality of the analyses and the agreement was good. Elements are detected down to a concentration of 0.01 mg/l which is appropriate for those elements in the simulated leachate and a number of other elements released in significant concentrations by the leaching of PFA. A number of trace elements will be released into solution from PFA in concentrations lower than 0.01 mg/l and for their determination either ICP-MS or furnace AAS would have been employed if the experimental work has not been essentially concerned with the possible interaction between simulated leachate and PFA. The As, Hg, Se and Mo concentration were determined by ICP and AAS attached with hydride generating system. There was general agreement but the ICP gave more consistent results and are quoted in Table 2. Anions were measured using Dionex 2000i Ion Chromatography.

The composition of the PFA was also determined before and after the leaching experiments. The samples were analysed by X-ray fluorescence spectrometry using lanthanum borate fused discs for major and trace elements.

RESULTS AND DISCUSSION

A number of authors have investigated the leaching behaviour of PFA using distilled water and dilute acids (Brown *et al.*, 1976; van der Sloot *et al.*, 1982;Hjelmar,

1990) and demonstrated significant concentrations in solution of Ca, Mg, Na, K, SO_4^{2-} , Cl^- , As, Cr_{total} , Mo, Se, V and B. The results generated in the present study should be comparable with previous batch studies for the fresh PFA, but not necessarily for the weathered PFA. In previous studies (van der Sloot *et al.*, 1982; Hjelmar, 1990) the effect of weathering has been investigated in the laboratory and in field trials that were, however, of short duration compared with the length of time the PFA used in the present project has been subjected to natural weathering. Although the batch leaching using distilled water was undertaken primarily as a control on the experiments with the simulated leachate the results, nevertheless (a) allow a comparison with previous work on the leaching of the fresh PFA, (b) provide information on the leaching of weathered PFA, which should correspond to predicted long-term behaviour based on the leaching of fresh PFA, and (c) provide laboratory information on weathering to compare with the field studies being undertaken at Drax and Meaford.

Batch Leaching of Fresh Drax PFA with Distilled Water

The batch leaching concentrations for fresh Drax PFA with distilled water are shown on Table 2. (Samples Dfd1-4 for successive leaches). The major elements present in PFA most readily leached from the fresh PFA are Ca, Na, and K in order of concentration and S (as SO_4^{2-}). Al and Si are major components of the ash and are present in the leachates, but only at concentrations of a few parts per million. Other elements are present in solution at comparable concentrations, but these are trace elements in the ash, and therefore a significantly higher proportion of these elements is released by leaching. Notable in this group of elements are B and Mo.

In successive leaches (Dfd2-4 Table 2) the elements most readily leached from the ash in the first treatment are present at much lower concentrations. Approximately 80% of the total amount of the soluble Ca, Na, K and S (as SO_4^{2-}) is liberated in the first treatment. Other elements which clearly exhibit this pattern are B, Cr_{total} , Cu, Li, Ni, Hg, Mo and Cl^- . These elements are concentrated on the surface of the PFA particles (Theis and Wirth, 1977; Hulett *et al.*, 1980; Clarke and Sloss, 1992). There are, however, elements which differ markedly in behaviour and comparable amounts are dissolved with each leaching. Falling into this group are Mg, Al, Ba, Si, V, As, and Se. The implication is that these elements are present in less readily soluble components in the ash and presumably this is essentially the glass. Elements intermediate in leaching behaviour are Fe, Co, Pb, Sr, Zn, and Zr.

Batch Leaching of Weathered Drax PFA with Distilled Water

This sample of Drax PFA was deposited near-surface on the Barlow mound seventeen years ago and throughout this period has been subjected to weathering due to the infiltrating porewater. Loss of the readily soluble elements would therefore be anticipated. The results on Table 2 (dwd 1) show that this is indeed the case. The concentrations for Ca, Na, K, SO_4^{2-} , B, Cr_{total} , Cu, Li, Ni, Hg, and Mo are all much lower with some of the trace elements below detection limits. One element which is present at a higher concentration in the weathered PFA is N (as NO_3^-) and the most likely explanation is derivation from fertilizers applied at the surface. Concentrations fall with each successive treatment with distilled water (Dwd 2-4). In part this can be attributed to a contribution from original porewater contained within the PFA. Partial dissolution of secondary reaction products and primary glass are also possible contributors. The essential point is, however, that for the readily soluble elements concentrations recorded for the weathered PFA are comparable with these achieved by successive leaching of the fresh PFA.

Based on the leaching results for the fresh PFA it would be anticipated that the elements Mg, Al, Ba, Si, V, As and Se would be leached from the weathered PFA in comparable concentrations to the fresh PFA both in the initial and subsequent extractions. This is the case with the exception of Mg and Se, both of which show a greater decrease with each leaching, but Se is close to and below the detection limit.

The other group of elements identified as more intermediate in character from the fresh PFA leaching namely Fe, Co, Pb, Sr, Zn and Zr are present at low concentrations close to and below detection limits which would have been anticipated.

Batch Leaching of Weathered Meaford PFA with Distilled Water

The results obtained from this material from Meaford (mwd 1-4, Table 2) are closely comparable to those obtained from the weathered PFA from Drax. Not only are the trends with each extraction very similar but so too are absolute concentrations. Although the total amount extracted is very much reduced compared with the fresh PFA, with some elements undetected, nevertheless, there are trace elements which are extractable from the PFA even after natural weathering for over 20 years. Both As and B are in this category and Se as well.

The Meaford sample is believed to be older than that

Table 2. Analytical results of the eluate from the batch leaching test with deionised water (Concentrations in mg/l unless indicated)df: Drax fresh, dw: Drax weathered, mw: Meaford weathered PFA. 1,2,3 and 4 denote successive treatment with water.

	pH	Pe	C mS	Ca	Na	K	Mg	Fe	Al	B	Ba	Cd	Co	Cr	Cu
dfd1	9.34	8.39	1130.0	173.1	42.1	21.3	0.99	0.25	3.67	2.77	0.30	0.00	0.05	0.30	0.10
dfd2	9.97	7.87	150.8	19.3	4.9	2.8	1.5	0.04	1.37	0.93	0.29	0.00	0.02	0.06	0.02
dfd3	7.12	7.92	242.0	35.3	2.9	1.9	2.12	0.04	0.07	0.52	0.89	0.00	0.02	0.04	0.01
dfd4	8.80	7.20	70.0	10	1.5	0.4	1.4	0.10	1.72	0.24	0.25	0.00	0.02	0.03	0.01
dwd1	7.26	8.42	215.0	26.6	4.3	2.4	1.98	0.02	0.60	0.18	0.54	0.05	0.00	0.01	0.00
dwd2	7.60	7.98	102.4	10.5	2.6	0.5	0.78	0.02	0.79	0.08	0.40	0.00	0.00	0.00	0.00
dwd3	7.67	7.47	61.0	9.4	1.8	0.3	0.57	0.01	0.80	0.06	0.24	0.00	0.00	0.00	0.00
dwd4	8.10	7.23	102.9	8.6	1.1	0.1	0.47	0.01	1.07	0.03	0.17	0.00	0.00	0.00	0.00
mwd1	7.08	8.69	193.0	21.1	3.6	3.6	1.27	0.14	0.37	0.18	0.28	0.16	0.00	0.06	0.05
mwd2	7.40	7.94	111.5	10.3	4.2	0.4	0.71	0.03	0.28	0.15	0.72	0.01	0.00	0.00	0.00
mwd3	7.26	7.46	60.5	9.4	2.1	0.7	0.62	0.08	0.75	0.08	0.23	0.01	0.00	0.00	0.00
mwd4	7.73	7.17	65.3	8.8	3.1	0.2	0.55	0.06	0.74	0.08	0.45	0.00	0.00	0.35	0.00
	Li	Ni	Pb	Si	Sr	V	Zn	Zr	As	Hg	Se	Mo	Cl ⁻	NO ₃ ⁻	SO ₄
dfd1	0.74	0.18	0.15	1.55	0.48	0.36	0.18	0.26	0.14	0.22	0.15	1.12	6.10	0.75	492.43
dfd2	0.10	0.02	0.10	1.86	0.10	0.26	0.02	0.12	0.12	0.03	0.15	0.23	2.30	0.73	34.64
dfd3	0.06	0.00	0.05	3.38	0.17	0.21	0.15	0.09	0.49	0.03	0.11	0.09	0.46	7.23	22.1
dfd4	0.02	0.02	0.05	1.56	0.05	0.24	0.02	0.07	0.34	0.14	0.14	0.04	0.34	2.59	19.7
dwd1	0.03	0.00	0.00	1.25	0.14	0.11	0.06	0.01	0.31	0.01	0.05	0.00	7.31	24.29	17.52
dwd2	0.01	0.00	0.00	1.08	0.06	0.12	0.06	0.00	0.29	0.00	0.00	0.00	5.21	1.22	3.99
dwd3	0.01	0.00	0.00	1.16	0.04	0.11	0.03	0.00	0.30	0.01	0.00	0.00	1.65	1.57	1.50
dwd4	0.00	0.00	0.00	1.15	0.04	0.09	0.01	0.00	0.22	0.00	0.01	0.00	0.54	0.57	1.26
mwd1	0.02	0.03	0.00	1.55	0.17	0.07	0.12	0.01	0.18	0.01	0.07	0.00	3.20	2.37	21.08
mwd2	0.00	0.00	0.00	1.78	0.09	0.09	0.05	0.00	0.17	0.03	0.06	0.00	3.61	0.52	4.90
mwd3	0.00	0.00	0.00	1.69	0.07	0.09	0.04	0.00	0.18	0.00	0.08	0.00	1.50	0.59	2.30
mwd4	0.00	0.00	1.41	1.26	0.07	0.07	0.02	0.00	0.18	0.00	0.04	0.03	2.90	1.30	1.41

form Drax but there is no obvious evidence that one is more weathered than the other. Indeed the very similar extraction performance suggests very similar weathering histories.

Batch Leaching of Fresh Drax PFA with Simulated Leachate

The primary objective of the experimental work was to determine if there was reaction between PFA and a simulated leachate leading to a loss of elements from solution. The natural weathering of PFA will lead to the formation of reaction products, including clay minerals which are capable of removing elements from solution. The response of the fresh and weathered PFA samples to the simulated leachate should therefore differ.

The analyses of the solutions after treatment with simulated leachate followed by water leaching are given on Table 3. The composition of the simulated leachate is also shown on Table 3. One important difference to note in behaviour is that the resulting solutions are acid compared with the alkaline solutions using only distilled water (Table 2). The Drax fresh ash (dfs 1, Table 3)

yields high solution concentrations of Ca, Na, K and S (as SO₄²⁻), which exceed the concentration of the simulated leachate. The differences are broadly comparable with the behaviour of the ash with water. The leachate does, however, contain organic acids and this could account for the enhanced dissolution of Ca. The same explanation applies to Mg which is present in the simulated leachate, but concentrations after reaction are higher, which contrasts with the behaviour of this element in water leaching.

One element which does decrease significantly after reaction is Fe. The solution concentration is reduced by approximately 50%. The other elements present in the leachate as major components are Cd, C_{Total}, Cu, Li, Ni, Zn and Hg. In all cases concentrations after reaction are comparable to the starting composition with possibly only Cd decreasing suggesting reaction with the PFA.

Si and Al are present in only trace concentrations in the leachate but after reaction solution concentrations are greatly in excess of amounts liberated with distilled water. As for the greater dissolution of Mg this is attributed to the more aggressive nature of the synthetic

Table 3. Analytical results of the eluate from the batch leaching test with synthetic leachate (Concentrations in mg/l unless indicated. df=Drax fresh PFA. dw=weathered Drax PFA, mw=Meaford weathered PFA. 1 indicates treatment with eluate. 2, 3 and 4 are successive treatments with synthetic leachate).

Syn. Lea.	4.55	9.10	3550	615.9	1032.2	734.6	86.99	122.96	0.12	0.23	0.04	121.18	79.78	117.57	19.44
dfs1	4.80	10.48	15530	1038.3	1046.9	745.9	165.69	64.54	24.79	6.00	0.22	125.86	79.04	109.54	18.99
dfs2	5.31	8.98	1060	71.3	69.4	34.4	12.19	0.36	0.72	0.67	2.08	4.80	1.80	3.16	0.99
dfs3	5.92	7.78	98	9.3	5.6	3.5	1.33	0.00	0.04	0.19	0.76	0.38	0.40	0.24	0.06
dfs4	6.74	7.25	36	3.1	1.3	0.7	0.54	0.02	0.03	0.06	0.47	0.04	0.23	0.02	0.01
dws1	4.75	10.55	14400	888.3	1034.8	731.2	102.46	65.93	16.65	0.65	0.72	117.18	74.23	103.23	19.45
dws2	5.15	8.99	1123	65.8	79.6	42	9.38	0.90	0.98	0.25	1.24	5.71	2.17	3.61	1.20
dws3	5.94	7.80	105	7.5	5.6	3.8	1.4	0.12	0.02	0.13	0.74	0.56	0.39	0.30	0.10
dws4	6.81	7.23	31	2.1	1.4	0.8	0.6	0.07	0.00	0.08	0.26	0.09	0.14	0.03	0.03
mws1	5.00	10.49	15720	1363.9	1023.9	727.7	121.14	51.31	33.60	0.83	0.48	103.10	65.57	67.57	18.89
mws2	5.51	8.91	1490	128.6	85.8	58.4	16.59	1.35	0.24	0.22	0.99	3.95	1.86	1.33	1.32
mws3	6.20	7.87	210	18.9	9.8	8.7	2.93	0.21	0.00	0.16	0.73	0.48	0.53	0.15	0.14
mws4	6.78	7.43	68	6.0	2.7	2.6	1.26	0.28	0.00	0.11	1.30	0.10	0.30	0.03	0.03
	Mn	Ni	Pb	Si	Sr	Ti	V	Zn	As	Hg	Se	Mo	Cl ⁻	NO ₃ ⁻	SO ₄
Syn. Lea.	0.18	109.40	0.22	0.81	0.16	0.05	0.11	107.60	0.27	13.85	0.33	0.68	1973.49	20.67	419.25
dfs1	2.96	114.18	0.35	51.84	1.46	0.14	0.28	112.17	0.65	14.32	0.50	1.00	1005.95	43.30	869.68
dfs2	0.81	4.48	0.00	5.05	0.22	0.01	0.02	5.52	0.03	0.49	0.05	0.01	74.78	3.31	38.89
dfs3	0.12	0.23	0.01	2.28	0.08	0.00	0.01	0.71	0.01	0.01	0.04	0.00	4.22	0.79	6.08
dfs4	0.03	0.03	0.01	1.51	0.05	0.01	0.02	0.13	0.01	0.01	0.02	0.12	2.47	2.73	5.28
dws1	1.40	108.54	0.16	23.32	1.32	0.08	0.16	102.78	0.59	12.06	0.43	0.75	1065.44	31.42	408.30
dws2	0.48	5.76	0.00	6.57	0.18	0.00	0.02	6.85	0.02	0.58	0.05	0.01	78.06	1.93	21.00
dws3	0.08	0.51	0.00	2.85	0.09	0.00	0.01	0.88	0.03	0.01	0.04	0.00	5.77	0.46	5.05
dws4	0.02	0.07	0.00	2.23	0.02	0.00	0.01	0.21	0.01	0.01	0.06	0.00	0.88	0.87	3.25
mws1	3.56	102.97	0.23	54.89	5.05	0.13	0.15	94.60	0.56	10.89	0.50	0.70	1208.92	143.27	387.50
mws2	0.78	6.15	0.00	11.62	0.52	0.01	0.02	6.16	0.05	0.37	0.01	0.01	83.02	0.91	24.36
mws3	0.17	0.74	0.00	8.91	0.17	0.00	0.01	0.95	0.00	0.03	0.05	0.00	7.87	0.89	11.29
mws4	0.05	0.15	0.00	7.35	0.07	0.00	0.01	0.30	0.02	0.01	0.07	0.00	1.41	0.61	8.11

Table 4. Composition of PFA before and after treatment with distilled water (d) and synthetic leachate (s). Concentrations of major elements are percentages and trace elements are parts per million. PFA samples indicated as follows : DF=Drax fresh, DW=Drax weathered, MW=Meaford weathered. The suffixes D and S indicates composition after treatment with deionised water (D) and synthetic leachate (S).

	L.O.I.%	SiO ₂ %	TiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ (T)%	MnO ₂ %	MgO%	CaO%	Na ₂ O%	K ₂ O%	P ₂ O ₅ %	SO ₃ %	Mn
DF	0.92	53.01	0.95	26.58	7.39	0.06	1.69	1.86	1.70	3.89	0.24	0.48	498
DFD	2.55	52.92	0.94	26.63	6.95	0.06	1.70	1.43	1.53	3.85	0.24	0.06	467
DFS	2.49	53.70	0.97	26.79	7.61	0.06	1.58	1.10	1.56	3.96	0.23	0.03	476
DW	5.11	51.42	0.89	25.50	9.01	0.06	1.48	1.30	1.33	3.64	0.20	0.08	443
DWD	4.95	50.55	0.91	26.61	8.89	0.06	1.52	1.25	1.33	3.78	0.19	0.14	461
DWS	5.31	49.94	0.94	26.65	8.59	0.06	1.50	0.81	1.27	3.72	0.23	0.01	419
MW	8.31	43.81	0.80	24.18	14.04	0.14	1.41	3.19	0.78	2.14	0.30	0.18	1071
MWD	8.26	44.93	0.82	25.03	13.03	0.13	1.39	2.95	0.74	2.20	0.32	0.19	975
MWS	7.64	45.53	0.85	25.41	13.32	0.13	1.29	1.53	0.83	2.25	0.33	0.09	987
	NI	Cu	Zn	Rb	Sr	Y	Zr	Nb	Ba	Pb	V	Cr	Total
DF	109	162	110	180	314	48	190	20	1134	67	249	125	99.42
DFD	103	151	112	175	301	47	190	14	1158	68	252	129	100.14
DFS	112	269	134	178	296	49	194	18	1100	68	235	174	99.35
DW	113	179	113	167	251	46	179	18	771	84	272	129	100.09
DWD	133	194	125	173	271	56	183	17	856	95	285	146	100.29
DWS	133	401	157	178	262	50	182	17	865	98	296	212	99.11
MW	143	173	800	107	323	53	168	13	1071	175	244	105	98.87
MWD	142	176	808	109	322	49	166	14	1030	183	249	106	98.64
MWS	224	731	1039	115	296	54	175	14	1105	220	264	250	100.16

leachate. This effect is also seen for elements such as B, As and Se.

Analysis of the solutions after reaction confirms the leaching pattern established using only water in the batch leaching, with greater dissolution being observed in most cases. There is loss of Fe from solution and possibly Cu but for other elements concentrations were high initially and remain so. The experimental conditions have a high ratio of solution (500 mls) to sample (50 gms) and significant reaction with the PFA might not be detected in the solution analysis. This difficulty can be resolved by analysis of the PFA before and after reaction.

The analyses of the PFA are given in Table 4. Comparison of the PFA after reaction with the leachate and with distilled water shows an increase in Cu, Cr, Zn and possibly Ni. There is also an increase in Fe. The analysis of the PFA therefore confirm and extend the conclusions based on the analysis of the solutions. There is reaction between synthetic leachate and PFA with elements extracted from solution.

The PFA analysis (samples DF, DFD and DFS in Table 4) also demonstrates major changes for Ca and S (expressed as SO_3) showing that leaching removes an important fraction of the total. This applies to Na to a lesser extent and to K not at all.

Batch Leaching of Weathered Drax with Simulated Leachate

Comparing weathered and fresh Drax PFA with water leaching demonstrated greater loss into solution from the fresh ash. The same relationship holds when comparing the performance of the two materials with simulated leachate, (dws1 and dfs1 Table 3). Only in the case of Ca, however, is the amount leached significantly greater than the initial concentration in the leachate. Na, K and S (as SO_4^{2-}) are all present at concentrations close to that of the leachate. For those elements not present in the leachate the loss into solution is greater than for distilled water. (Mg, Al, B, Ba, Si and Sr). The same relationship was noted with the fresh ash.

The elements Fe, Cr_{total} , Cu, and possibly Zn and Hg show a decrease in concentration in solution after treatment with the weathered PFA (Table 3). In order to substantiate the conclusion of reaction and loss from solution the analyses of weathered Drax PFA after treatment with water and leachate are compared (samples DWD and DWS Table 4). There are increases in Cr_{total} , Cu, and Zn, after reaction with the leachate. The gain in Fe by the PFA noted in the solution analyses is not apparent in the PFA analyses (Table 4) because

Fe is a major component of the ash and the gain is relatively small. Nevertheless the analyses of the PFA and of the solutions after reaction do demonstrate reaction leading to loss of elements from solution.

Batch Leaching of Weathered Meaford PFA with Simulated Leachate

The solution analyses for the Meaford sample are shown in Table 4 (MWS1 - MWS4). There is close agreement with the results obtained from the Drax weathered sample. There is major dissolution of Ca but Na, K and S (as SO_4^{2-}) are close to initial leachate concentrations.

As noted in previous sections the low pH leachate leads to greater dissolution compared with water. Elements not present in the leachate, or strictly present in only trace amounts, are observed after the batch leaching in high concentrations. In this category are Mg, Al and Si.

A key observation in this work is the reduction in concentrations of Fe, Cd, Cr_{total} , Cu, Ni, Zn and Hg in the leachate after reaction with the weathered Meaford PFA (MWS1 Table 4). Compared with the weathered Drax PFA there is a greater fall in concentrations and two additional elements show significant decreases, namely Cd and Ni. These findings are confirmed from the analyses of the weathered Meaford PFA which is higher in Fe, Cr_{total} , Ni, Cu and Zn after treatment with the leachate (sample MWS compared with MW, Table 4). Evidence of reaction is therefore obtained for these elements both by gain onto PFA and loss from solution. The magnitude of the changes for these elements is weathered Meaford PFA > weathered Drax PFA > fresh Drax PFA. This coincides with the age and presumably the extent of weathering and formation of secondary minerals.

CONCLUSIONS

1. In batch leaching experiments using a simulated landfill leachate and weathered PFA elements are removed from solution. Decreases in solution concentrations (measured by ICP) have been recorded for Fe, Cd, Cr_{total} , Cu, Ni, Zn and Hg. Confirmation of the increases on the PFA has been obtained by analyses of the PFA (Cd and Hg were not included within the XRF analyses).
2. The order of metal retention by the three samples is Meaford > weathered Drax > fresh Drax. It is concluded that more weathered the sample the more effective it is at removing elements from solution.
3. Batch leaching of fresh PFA with distilled water

confirms the results of other workers. However, little work has been undertaken previously on weathered PFA and the batch leaching using distilled water demonstrates that elements continue to be released into solution over long periods, albeit it at a very much reduced dissolution rate.

4. The rate of dissolution provides evidence of the location of the elements in the ash. Ca, Na, K, S, B, Cr_{total}, Cu, Li, Ni, Hg, Mo and Cl⁻ are readily leached from the ash and there is evidence of a surface association. Mg, Al, Ba, Si, V, As and Se are apparently present in less readily soluble components of the ash and presumably this is essentially the glass. Intermediate in behaviour are Fe, Co, Pb, Sr, Zn and Zr.

5. The simulated leachate contains organic acids with a pH of 4.5. Compared with the distilled water there is evidence of greater dissolution of a number of elements from the PFA. These are elements not present in the synthetic leachate.

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풍화 석탄연소 고형폐기물(Pulverised Fuel Ash)의 중금속 제거가능성 :

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이 상 훈

요 약 : 영국의 2개 화력발전소로부터 석탄연소 폐기물 시료를 17년, 약40년 풍화된 것 그리고 풍화되지 않은 것의 구분으로 각각 채취하였다. 이 시료들과 증류수, 인공 침출수등을 이용, 배치 실험을 실시하였다. 풍화되지 않은 시료의 증류수를 통한 실험에서는 Ca, Na, K, S, B, Cr, Cu, Li, Ni, Mo 그리고 Cl⁻ 등 원소가 다량으로 방출되는 것이 관찰되었으며 이는 이들 원소들이 주로 표면에 수반된다는 증거가 된다. Mg, Al, Ba, Si, V, As 그리고 Se 등은 이러한 다량방출을 하지 않는바 이들 원소들은 입자 표면보다는 PFA 입자의 유리질에 수반되는 것으로 생각된다. 풍화 PFA시료를 통한 실험에서는 유리질과 같은 상온에서 불안정한 상에 수반되는 용융성원소들이 용액으로 방출됨이 증명되었다. 인공 침출수를 이용한 실험에서는 Fe, Ca, Cr, Cu, Ni, Zn 그리고 Hg등이 제거되는것이 관찰되었으며 이는 용액으로부터 제거되어 고체 PFA의 성분에서 증가하는것을 통하여도 확인된다. 중금속 제거정도는 Meaford>Drax 풍화시료>Drax 신선한 시료의 순이며 이는 풍화의 정도와도 일치한다. 즉 풍화를 많이 받은 시료에서 더 많은 중금속이 제거되는 결과를 보여준다.