

Burning of Hazardous Wastes as Co-Fuel in a Cement Kiln - Does it Affect the Environmental Quality of Cement ?

Kåre Helge Karstensen

The Foundation for Scientific and Industrial Research SINTEF SI, P.O. Box 124 Blindern,
N-0314 Oslo, NORWAY.

SUMMARY

In Norway liquid organic wastes is commonly used as a supplementary fuel to coal in the production of cement. Studies during several years has proven that this is an environmental sound practice. The organic compounds in the waste are safely destructed and the heavy metals are to a high extent retained in the clinker. This paper evaluates if any additional content of heavy metals causes any enhanced leaching compared to clinker produced without waste fuel and compares results from different regulatory leaching test to see if they are in accordance.

1 INTRODUCTION

Cement kilns offer an excellent alternative for destruction of hazardous organic waste. The advantages of a cement kiln are the high temperature (1400°C - 2000°C) and long residence time in the rotary kilns (1, 2, 3). Furthermore, when burning halogenated organics, a large mass of alkaline cement clinker absorbs and neutralizes the acidic stack gases. Because of the high energy requirement of cement production, the combustion of hazardous waste containing a high calorific value (i.e. waste oil and solvents) results in significant fuel savings. So far much attention has been given to assess the potential environmental impacts of this practice, i.e. emission studies from cement production plants. Studies during several years has proven that this is an environmental sound practice (4, 5). The organic compounds in the waste are safely destructed and the heavy metals are to a high extent retained in the clinker. There is therefore considerable interest in whether the use of wastes as a supplementary fuel has any effect on the environmental quality of cement. So far has this usually been evaluated by performing the US TCLP test (6). There is, on the other hand, performed studies which has been focusing on leaching from different materials stabilized or mixed with cement (7, 8, 9, 10).

This paper presents results from studies where different hazardous wastes was used as supplementary fuel together with coal. The cement kiln was operated in a dry process mode. The studies includes also investigations from normal cement production using coal only. The

wastes, constituted about 15 % of the total fuel consumption, was pumped into the cement kiln as a liquid or a suspension and contained chlorinated organic compounds, as chlorinated benzenes and polychlorinated biphenyls (PCB), and heavy metals.

Several earlier studies has indicated that heavy metals in fuel and raw materials will be retained in the clinker, i.e. the product of the cement plant (11, 12, 13), and not discharged from the plant. The aim of this study was in two parts; firstly to evaluate if any additional content of heavy metals in clinker causes any enhanced leaching compared to clinker produced with coal only, and secondly, to compare the results from different regulatory leaching test to see if they were in accordance.

2 EXPERIMENTAL

Several full scale trial burns were performed in this project, with and without waste fuel. Emission samples and samples of solid process solids were continuously collected over several days in each trial, and process parameters were monitored. To evaluate the fate of the constituents in the waste fuel, samples of raw-materials, fuel batches, coal, precipitator ash, stack-outlets and clinker were thoroughly analyzed for organic and inorganic constituents.

2.1 CHEMICAL ANALYSIS OF PROCESS SAMPLES

All the elements were analysed with ICP-AES after high-pressure acid decomposition (14), with the exception of mercury which was analysed with AAS cold vapor technique. Some of the samples were also analysed with XRF. ICP is not adequate with regards to the detection limits for several of the trace elements and further investigations will be performed with more appropriate techniques. In table 1 are the samples which were tested with different leaching tests listed.

Table 1
Summary of samples tested with leaching tests

Designation	Description
D147	Mortar specimen made of cement produced with coal only
D148	Mortar specimen made of cement produced with coal and waste fuel
5/5	Clinker made of cement produced with coal only
19/5	Clinker made of cement produced with coal and special waste fuel
22/5	Clinker made of cement produced with coal and PCB-waste fuel
6B	Electro precipitator ash produced with coal and waste fuel

Two of the clinker samples, produced with and without waste fuel, were prepared as mortars according to EN 196-1 (15), i.e. 450 gram of cement (approximately 430 gram of grinded clinker is mixed with approximately 20 gram of gypsum), 1350 gram of sand and 225 gram of water were mixed and cured for 24 hours under 95 % relative humidity at 20°C. Prior testing, the specimens was stored for 28 days under 100 % relative humidity at 20°C. Table 2 lists the characteristics of the mortar specimens.

Table 2
Characteristics of mortar specimen

	D147	D148
Dimensions (cm)	4 x 4 x 16	4 x 4 x 16
Curing time (days)/conditions	1 / 20°C, 95% RH 28 / 20°C, 100% RH	1 / 20°C, 95% RH 28 / 20°C, 100% RH
Compressive strength (MPa)	50,3	49,9
Bend strength (MPa)	7,8	7,6
Composition	450 gram of cement, 1350 gram of sand and 225 gram of water	

The mortar specimens are both in the normal range with regards to compressive strength and bend strength, and there is no significant difference between the specimens.

The other four samples, two clinker samples produced with coal and waste fuel, one clinker sample produced with coal only and one electro precipitator ash produced with coal and waste fuel, were tested without further preparation. The elemental composition of the samples are listed in table 3.

As can be seen from table 3, is the difference in composition in the mortar samples D147 and D148 marginal, with the exception of Cr, Cu and Zn which are statistical significant higher in D148. This mortar is made of clinker produced with coal and special waste fuel, and the additional elemental content is probably due to enriched in these elements in the waste fuel compared to coal. Table 4 list the elemental composition of fuels and raw material. This tendency is even more pronounced in the clinker samples.

The difference in composition between the precipitator ash 6B and the other samples are marginal, although we can see some tendencies to enrichment of volatile elements like Tl in the ash. The more volatile species will condense on dust and ash particles further out in the plant and is trapped in the electro precipitator (16).

Table 3
Elemental composition of samples (listed in table 1)

	D147	D148	5/5	19/5	22/5	6B
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
Al	10000	10000	11000	10400	26300	15700
As	<10	<10	<10	<10	<10	<10
B	<10	<10	<10	<10	<10	<10
Ba	80	90	140	135	135	70
Be	<2	<2	<2	<2	<2	<2
Ca	120000	150000	300000	310000	320000	313000
Cd	<4	<4	<4	<4	<4	<4
Co	4,5	5,5	10	13,5	14	12
Cr	25	34	77	90	100	52
Cu	27	35	24	50	48	50
Fe	8000	9100	16000	16000	17000	18200
Hg	NA	NA	0,12	0,16	0,21	0,19
K	2000	3000	9000	8800	10000	11000
Li	35	40	72	70	73	65
Mg	4500	5400	9300	9000	8500	10800
Mn	120	150	350	360	370	250
Mo	<4	<4	<4	<4	<4	<4
Na	2000	1700	3500	3400	3400	3200
Ni	12	18	30	30	35	20
P	95	100	250	290	260	220
Pb	<17	<17	<17	35	30	40
Sb	<17	<17	<17	<17	<17	<17
Sc	<2	<2	6	6	6	4
Se	<20	<20	<20	<20	<20	<20
Si	90000	90000	52000	49000	47000	32000
Sn	<15	<15	30	30	36	<15
Sr	220	230	650	600	610	400
Ti	580	650	1300	1400	1350	950
Tl	<10	<10	<10	<10	<10	300
V	20	22	54	55	56	25
Zn	19	28	39	75	68	42

2.2 CHEMICAL ANALYSIS OF SAMPLES OF FUEL AND RAW MATERIAL

The elemental composition of fuel samples and raw material are listed in table 4. The samples are so far only analysed with ICP-AES and XRF. As can be seen from the table is the difference in sample composition marginal, with the exception of Cr, Cu, Hg, and Zn which is significant higher in the waste samples, and Tl and V which is higher in the coal. When wastes are used as a supplementary fuel it constitutes maximum 15 % of the total fuel consumption, the rest is coal. That implies the additional heavy metals in the wastes will to a high degree be diluted in the process.

Table 4
Elemental composition of fuel and raw material

	Coal	Special waste	PCB waste	Raw material
	mg/kg	mg/kg	mg/kg	mg/kg
Al	14000	1200	1000	15000
As	<10	<3	<3	<10
B	88	21	10	<10
Ba	320	740	800	13
Be	<2	<1	<1	<2
Ca	15000	2100	1100	310000
Cd	<4	<4	<1	<4
Co	7,7	19	122	7
Cr	20	138	200	62
Cu	15	1110	300	14
Fe	7200	3700	3200	14600
K	3000	<20	<20	1200
Hg	0,082	0,55	1,43	0,050
Li	60	18	35	70
Mg	1700	1200	1100	10400
Mn	178	160	200	250
Mo	<4	43	20	<4
Na	900	2600	1800	2150
Ni	34	22	15	15
P	300	310	450	154
Pb	<17	675	1000	<17
Sb	<17	<15	<15	<17
Sc	<2	<1	<1	<2
Se	<20	<10	<10	<20
Si	14000	6000	4000	51000
Sn	<15	40	50	<15
Sr	220	29	35	420
Ti	940	8800	5600	880
Tl	15	<10	<10	<10
V	160	5	7	25
Zn	35	2150	1800	27
F	202	90	71	489
Cl	160	6375	14800	90
S	7720	2885	1740	4240

2.3 LEACHING TESTS

As can be seen from table 3 is the additional content of heavy metals in the samples produced with waste as fuel small because of dilution in the process. To evaluate if this small additional content of heavy metals in clinker causes any enhanced leaching compared to clinker produced with coal only several regulatory and standard test were performed. To get

a basis of knowledge with regards to future applicability of any of the tests, is it necessary to compare the results from different regulatory leaching test to see if they were in accordance.

Following leaching tests were performed on the samples listed in table 1: the Dutch NVN 5432 tank leaching test, NVN 2508 column test, NVN 2508 serial batch test and NVN 2508 availability test, the German DIN 38414 S4, the American EPA-TCLP and a modification of the German DIN test. In table 5 is the test scheme listed.

Table 5
Test scheme

Sample	Preparation	Leaching test	Number of leachates
D 147	Mortar	NVN 5432 Tank leaching test	8
	Crushed mortar	NVN 2508 Column test	7
	Crushed mortar	NVN 2508 Serial batch test	5
	Crushed mortar	NVN 2508 Availability test	1
	Crushed mortar	Modified DIN test	4
	Crushed mortar	DIN 38414 S4	1
	Crushed mortar	EPA-TCLP	1
D 148	Mortar	NVN 5432 Tank leaching test	8
	Crushed mortar	NVN 2508 Column test	7
	Crushed mortar	NVN 2508 Serial batch test	5
	Crushed mortar	NVN 2508 Availability test	1
	Crushed mortar	Modified DIN test	4
	Crushed mortar	DIN 38414 S4	1
	Crushed mortar	EPA-TCLP	1
5/5	Clinker	NVN 2508 Availability test	1
	Clinker	DIN 38414 S4	1
	Clinker	EPA-TCLP	1
19/5	Clinker	NVN 2508 Availability test	1
	Clinker	DIN 38414 S4	1
	Clinker	EPA-TCLP	1
22/5	Clinker	NVN 2508 Availability test	1
	Clinker	DIN 38414 S4	1
	Clinker	EPA-TCLP	1
6 B	Precipitator ash	NVN 2508 Column test	7
	Precipitator ash	NVN 2508 Serial batch test	5
	Precipitator ash	NVN 2508 Availability test	1
	Precipitator ash	Modified DIN test	4
	Precipitator ash	DIN 38414 S4	1
	Precipitator ash	EPA-TCLP	1

The tests uses different amounts of sample mass and generates leachates with different L/S ratio, and in order to compare the results between the tests, one have to take this into account. Those elements which are not detected in the leachates, are omitted in the tables, but is

mentioned in the text in each case. In table 6 is the detection limits for the actual elements listed. In each test, blind samples were run and analysed in the same way as real samples, and the results were taken into account.

Table 6
Detection limits (ICP-AES) of trace elements in leachates (mg/l)

Ag	<0,008	Cu	<0,004	Pb	<0,040
As	<0,026	Fe	<0,005	Sb	<0,042
B	<0,025	Hg	<0,0001	Sc	<0,002
Be	<0,001	Mn	<0,002	Se	<0,050
Cd	<0,011	Mo	<0,006	Sn	<0,036
Co	<0,005	Ni	<0,019	Ti	<0,002
Cr	<0,010	P	<0,090	Tl	<0,15

2.3.1 The Dutch NVN 5432 tank leaching test

In the NVN 5432 tank leaching test diffusion controlled (and surface wash off) leaching is measured. The mortar specimen is immersed in acidified demineralized water (5 times the volume of the specimen) without any stirring or agitation (17). The solution is renewed all together 8 times, i.e. after 0,25, 1, 2, 4, 8, 16, 32 and 64 days respectively. The solutions are filtered, pH and conductivity are measured. The solutions are finally conserved and analysed. The results are listed in table 7 and 8. On the basis of the results, diffusion coefficients can be measured (9). This can, under certain conditions, give a picture of the leaching process over time.

Table 7
Tank leaching test of sample D147

	0,25 day	1 day	2 days	4 days	8 days	16 days	32 days	64 days
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Al	<0,022	0,087	0,20	0,44	0,77	1,2	1,8	2
Ca	0,6	3	7	16	26	37	37	65
K	34	30	23	25	27	35	44	55
Li	<0,015	<0,015	<0,015	<0,015	0,023	0,025	0,025	0,044
Mg	<0,027	<0,027	<0,027	<0,027	0,060	0,037	0,087	0,030
Na	10	7,9	4,7	4,4	5,0	7,6	12	15
Si	5,3	9,5	7,2	9	10	12	15	13
Sr	<0,001	0,004	0,004	<0,004	0,038	0,074	0,14	0,28
pH	10,5	10,4	10,9	11,2	11,3	11,7	NA	NA
C uS/cm	145	137	94	95	104	520	NA	NA

Ag, As, B, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, P, Pb, Sb, Sc, Se, Sn, Ti, Tl and Zn was below the detection limit in alle the leachates.

Table 8
Tank leaching test of sample D148

	0,25 day	1 day	2 days	4 days	8 days	16 days	32 days	64 days
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Al	<0,022	0,123	0,123	0,123	0,81	0,97	1,8	1,9
Ca	1	4	9	17	28	125	48	64
K	39	32	21	21	23	22	35	46
Li	<0,015	<0,015	<0,015	0,018	0,022	0,045	0,025	0,037
Mg	<0,027	<0,027	0,032	0,041	0,055	0,037	0,043	<0,027
Na	11	8	5	4,1	4,5	6	10	14
Si	7	9	6	8	9	11	14	12
Sr	<0,001	<0,001	0,010	0,021	0,040	0,11	0,14	0,26
pH	10,8	11	11	11,2	11,4	11,6	NA	NA
C uS/cm	184	129	91	115	92	398	NA	NA

Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, P, Pb, Sb, Sc, Se, Sn, Ti, Tl and Zn was below the detection limit in alle the leachates.

As can be seen from tables 7 and 8 is it first of all the alkali metals Li, Na and K and the alkaline earth metals Ca, Mg and Sr, together with Al and Si, which is mobilised with time during the leaching test. This correlates well with the increase in pH and conductivity. There is almost no difference in leachability between the two samples, and the different content of heavy metals seems to have no significance.

2.3.2 The Dutch standard leaching test NVN 2508

The Dutch standard leaching test consists of three main parts: 1) a column test, 2) a serial batch shake test and 3) a test for the determination of the availability of elements for leaching under natural conditions (18).

2.3.2.1 Column test

In the column test approximately 800 grams of crushed sample (<3 mm) is percolated with water from the bottom to the top. 7 fractions are collected (L/S 0,1-10), the solutions are filtered, pH and conductivity are measured. Finally the leachates are conserved and analysed. The results are listed in table 9-11. The column test is used to assess short- and medium-term leaching, i.e. <50 years (8).

Table 9
Column test of sample D147 (crushed)

	L/S 0,1	L/S 0,5	L/S 1	L/S 2	L/S 3	L/S 5	L/S 10
	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Al	0,53	0,20	0,13	0,16	0,15	0,16	0,15
B	1,1	0,18	<0,025	0,15	0,14	0,11	0,09
Ba	0,43	0,67	1,1	1,2	1,1	1	0,71
Ca	360	470	725	1370	890	890	880
Co	0,074	0,051	0,029	0,032	0,013	0,010	0,009
Cr	0,43	0,21	0,063	0,050	0,022	0,015	0,018
Cu	0,019	0,006	<0,004	<0,004	<0,004	<0,004	<0,004
Fe	0,023	<0,005	0,019	<0,005	<0,005	0,003	0,002
K	3100	2000	720	230	80	19	8
Li	0,92	0,75	0,44	0,34	0,24	0,18	0,16
Mg	<0,027	<0,027	0,043	<0,027	<0,027	<0,027	<0,027
Na	870	570	210	60	28	8	3
Si	13	2,5	0,53	2,3	1,3	0,95	0,53
Sr	19	22	18	14	9,5	6,1	3,4
Zn	0,013	0,004	<0,002	<0,002	<0,002	<0,002	<0,002
pH	13,3	13,2	13,1	13,2	12,9	13	13
C mS/cm	27,0	19,3	11,8	9,2	8,4	8,0	7,8

Ag, As, Be, Cd, Hg, Mn, Mo, Ni, P, Pb, Sb, Sc, Se, Sn, Ti, Tl and V was below the detection limit in alle the leachates.

Table 10
Column test of sample D148 (crushed)

	L/S 0,1	L/S 0,5	L/S 1	L/S 2	L/S 3	L/S 5	L/S 10
	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Al	0,43	0,17	0,15	0,17	0,13	0,16	0,16
B	0,58	0,08	<0,025	0,19	0,07	0,08	0,10
Ba	0,36	0,70	1,2	1,4	1,3	1,1	0,83
Ca	340	510	660	1440	940	920	910
Co	0,086	0,060	0,036	0,038	0,012	0,010	0,008
Cr	0,82	0,40	0,13	0,09	0,04	0,03	0,03
Cu	0,030	0,010	<0,004	<0,004	<0,004	<0,004	<0,004
Fe	0,043	<0,005	<0,005	<0,005	<0,005	<0,005	<0,005
K	3300	1900	720	220	40	12	7
Li	0,97	0,71	0,47	0,36	0,22	0,18	0,16
Na	930	560	220	61	14	6	3,5
Si	7	2	2	3	0,84	0,92	0,62
Sr	19	24	21	17	9,5	5,2	2,8
Zn	0,02	<0,002	<0,002	<0,002	<0,002	<0,002	<0,002
pH	13,3	12,9	12	12,9	13,1	13	13
C mS/cm	29,9	18,2	11,1	9,5	8,6	8,2	7,8

Ag, As, Be, Cd, Hg, Mg, Mn, Mo, Ni, P, Pb, Sb, Sc, Se, Sn, Ti, Tl and V was below the detection limit in alle the leachates.

As can be seen from tables 9 and 10 are the alkali metals leached out first, together with some heavy metals. The concentration of Cr, Cu and Zn is higher in leachate from D148, but if this can be ascribed the higher content, is uncertain. The alkaline earth metals has another leaching pattern, with low mobility in the beginning, increasing to a maximum at L/S 1-2, and then decreasing.

Table 11
Column test of sample 6B

	L/S 0,1	L/S 0,5	L/S 1	L/S 2	L/S 3	L/S 5	L/S 10
	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Al	0,45	0,26	<0,022	<0,022	0,05	0,19	0,41
B	0,41	0,12	<0,025	0,07	0,06	0,05	0,06
Ba	0,088	<0,004	0,089	0,061	0,056	0,021	0,008
Ca	1070	900	860	1070	760	280	105
Cr	0,26	0,14	0,04	0,03	<0,010	<0,010	<0,010
Cu	0,06	<0,004	<0,004	<0,004	<0,004	<0,004	<0,004
K	1200	1100	800	170	50	18	7
Li	1,1	0,61	0,34	0,31	0,17	0,09	0,05
Mg	0,29	<0,027	<0,027	0,07	0,21	0,06	0,06
Mo	0,94	0,43	0,065	0,022	0,015	0,011	0,008
Na	200	760	65	12	6	3	1,6
Pb	<0,040	0,17	0,14	<0,040	<0,040	<0,040	<0,040
Si	14	16	18	22	21	18	14
Sr	7,4	6,6	3,9	2,8	2,3	0,87	0,30
Zn	0,014	<0,002	<0,002	<0,002	<0,002	<0,002	<0,002
V	0,068	<0,007	<0,007	<0,007	0,027	0,025	0,031
pH	12,64	12,25	11,71	11,27	11,21	10,84	10,80
C mS/cm	62,6	22,0	4,5	2,4	2,2	1,2	0,7

Ag, As, Be, Cd, Hg, Mn, Ni, P, Sb, Sc, Se, Sn, and Ti was below the detection limit in alle the leachates. The leaching of Tl will be further investigated.

The electro precipitator ash, sample 6B, shows the same picture as the crushed mortars, with the exception of lower concentrations of the alkali metals. We can also some leaching of Pb and Mo. If have to be noted that this precipitator ash is continuously feeded back into the process.

2.3.2.2 Serial batch test

In the serial batch test approximately 40 grams of crushed sample (<3 mm) is extracted 5 times with demineralized water at L/S ratio 20 for 24 hours each. 5 fractions are collected (L/S 20-100), the solutions are filtered and pH and conductivity are measured. Finally are the

leachates conserved and analysed. The results are listed in table 12-14. The serial batch test is used to get an impression of long-term leaching behaviour 50-500 years (8).

Table 12
Serial batch test of sample D147 (crushed)

	L/S 20	L/S 40	L/S 60	L/S 80	L/S 100
	ppm	ppm	ppm	ppm	ppm
Al	0,29	0,85	1,34	1,4	1,9
Ba	0,32	0,15	0,078	0,048	0,049
Ca	670	390	250	170	200
Cr	0,017	0,032	0,056	0,056	0,037
Fe	0,026	0,008	0,015	0,006	0,007
K	79	5	2	<1	1,6
Li	0,15	0,089	0,068	0,059	0,061
Mg	<0,027	<0,027	<0,027	0,046	0,048,
Na	24	2	0,9	0,7	1,4
Si	0,4	0,7	1,6	2,6	2,8
Sr	2,4	0,86	0,43	0,29	0,40
pH	13	12,6	12,2	11,4	12,2
C mS/cm	6,7	3,06	1,3	0,3	1,7

Ag, As, B, Be, Cd, Co, Cu, Hg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Ti, Tl and Zn was below the detection limit in alle the leachates.

Table 13
Serial batch test of sample D148 (crushed)

	L/S 20	L/S 40	L/S 60	L/S 80	L/S 100
	ppm	ppm	ppm	ppm	ppm
Al	0,23	0,65	1,1	1,1	1,6
Ba	0,35	0,19	0,092	0,054	0,052
Ca	740	480	270	180	220
Cr	0,035	0,058	0,11	0,13	0,088
Fe	0,025	0,006	<0,005	<0,005	0,008
K	80	6	1,3	<1	2,2
Li	0,16	0,10	0,071	0,068	0,066
Na	27	1,9	0,92	0,73	1,4
Si	0,39	0,49	1,1	2	2,4
Sr	2,52	0,90	0,44	0,28	0,37
pH	12,8	12,6	12,3	11,7	11,3
C mS/cm	6,3	4	2,3	0,53	0,4

Ag, As, B, Be, Cd, Co, Cu, Hg, Mg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Ti, Tl and Zn was below the detection limit in alle the leachates.

As can be seen from tables 12 and 13 increases the Al-concentration with time, to a higher extend than in the column test, in spite of the large dilution. Both alkali metals the alkaline earth metals decreases with time, which also correlates well with the decrease in pH and conductivity. Also in the batch tests are Cr higher in the leachates of D148.

Table 14
Serial batch test of sample 6B

	L/S 20	L/S 40	L/S 60	L/S 80	L/S 100
	ppm	ppm	ppm	ppm	ppm
Al	2	1,6	0,9	0,75	0,67
Ca	230	27	10	8,5	8,5
Cr	0,013	<0,010	<0,010	<0,010	<0,010
K	300	18	6	3	3,6
Li	0,094	0,022	<0,015	<0,015	<0,015
Mg	0,08	0,11	0,20	0,35	0,53
Na	47	2,2	0,7	0,5	0,6
Si	7	6	4	2,8	2,8
Sr	0,78	0,08	0,03	0,03	0,04
pH	9,3	8,2	7,9	7,9	7,9
C mS/cm	2	NA	NA	0,06	0,06

Ag, As, B, Ba, Be, Cd, Co, Cu, Fe, Hg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Ti, Tl and Zn was below the detection limit in alle the leachates.

In the leachate of sample 6B we can see the Al- and the Si-concentration is decreasing with time, in contrast to sample D147 and D148. This correlates well with the decrease and lower concentration of alkali metals and the alkaline earth metals, and also with the decrease in pH and conductivity.

2.3.2.3 Availability test

In the availability test 8 grams of crushed and sieved sample (<125 um) is added 800 ml acidified (the pH is kept at pH 7 by adding 1 M HNO₃) demineralized water and stirred for 3 hours. The solution is then filtered, and the sample is added 800 ml acidified (the pH is kept at pH 4 by adding 1 M HNO₃) demineralized water and stirred for another 3 hours. The two extracts are combined and analysed. The results are listed in table 15. The availability test is assumed to give a picture of the maximum leachability under natural conditions (8).

Table 15
Availability test of all samples

	D147	D148	5/5	19/5	22/5	6B
	ppm	ppm	ppm	ppm	ppm	ppm
Al	3,2	4,3	7	2,6	0,35	0,067
B	0,097	0,22	0,15	0,14	0,13	<0,025
Ba	0,37	0,26	0,53	0,58	0,44	0,025
Ca	770	750	1780	1830	1830	1360
Co	0,010	0,013	0,018	0,021	0,015	<0,005
Cr	0,062	0,12	0,26	0,33	0,37	<0,010
Cu	0,036	0,062	0,050	0,092	0,008	<0,004
Fe	0,040	0,051	0,15	0,015	<0,005	0,15
K	13	11	38	38	40	33
Li	0,14	0,14	0,23	0,23	0,22	0,15
Mg	27	26	57	54	51	6,5
Mn	0,26	0,28	0,20	0,11	0,027	0,90
Na	6	6	11	12	13	6,5
Ni	0,025	0,043	0,073	0,073	0,051	<0,019
Si	46	44	58	64	62	2
Sr	1,2	1,1	2,5	2,3	2,3	1,4
V	<0,007	<0,007	0,038	0,040	0,051	<0,007

Ag, As, Be, Cd, Hg, Mo, Ni, P, Pb, Sb, Se, Sn, Ti, Tl and Zn was below the detection limit in all the leachates.

2.3.3 Modified DIN test

In the modified DIN test 100 grams of crushed and sieved sample (<4 mm) is added 200 ml acidified (the pH is adjusted to pH 4 by adding HNO₃) demineralized water and rotated for 6 hours. The solution is then filtered, and the sample is added 800 ml acidified (the pH is adjusted to pH 4 by adding HNO₃) demineralized water and rotated for another 18 hours. The solution is then filtered, and the sample is added 4000 ml acidified (the pH is adjusted to pH 4 by adding HNO₃) demineralized water and rotated for another 23 hours. All the fractions (L/S 2-50) are filtered, pH and conductivity are measured, and the leachate is conserved and analysed. The sample is then added 1000 ml acidified (the pH is kept at pH 4 by adding HNO₃) demineralized water and stirred for 4 hours. The leachate is filtered, conserved and analysed. The results are listed in table 16-18. The modified DIN test is assumed to give a more detailed picture of the leachability with time than the German DIN test.

Table 16
Modified DIN test of D147 (crushed)

	LS 2	LS 10	LS 50	pH 4
	ppm	ppm	ppm	ppm
Al	0,20	0,21	0,65	12
Ba	0,64	0,61	0,14	1,2
Ca	530	850	430	5800
Co	0,028	0,012	<0,005	0,070
Cr	0,034	0,026	0,025	0,27
Fe	0,015	0,012	0,011	0,15
K	780	75	0,85	7
Li	0,40	0,21	0,13	0,43
Mg	<0,027	<0,027	<0,027	200
Mn	<0,002	<0,002	<0,002	2,3
Na	260	17	0,8	9
Ni	<0,019	<0,019	<0,019	0,25
P	<0,090	<0,090	<0,090	0,22
Si	0,4	0,2	0,5	76
Sr	11	5	0,54	4,7
Zn	<0,002	<0,002	<0,002	0,29

Ag, As, Be, Cd, Cu, Hg, Mo, Pb, Sb, Se, Sn, Ti, Tl and V was below the detection limit in all the leachates.

Table 17
Modified DIN test of D148 (crushed)

	LS 2	LS 10	LS 50	pH 4
	ppm	ppm	ppm	ppm
Al	0,18	0,22	0,50	10
Ba	0,66	0,63	0,16	0,96
Ca	540	4760	490	5000
Co	0,029	0,011	<0,005	0,079
Cr	0,058	0,040	0,045	0,55
Cu	<0,004	<0,004	<0,004	0,097
Fe	0,014	0,009	0,007	0,12
K	800	73	1	1,3
Li	0,38	0,21	0,13	0,37
Mg	<0,027	<0,027	<0,027	170
Mn	<0,002	<0,002	<0,002	1,8
Na	270	18	0,9	7
Ni	<0,019	<0,019	<0,019	0,24
P	<0,090	<0,090	<0,090	0,26
Si	0,35	0,25	0,41	70
Sr	11	4,8	0,57	3,5
Zn	<0,002	<0,002	<0,002	0,41

Ag, As, Be, Cd, Hg, Mo, Pb, Sb, Se, Sn, Ti, Tl and V was below the detection limit in alle the leachates.

We can clearly see the effect of keeping pH at 4 in table 16 and 17, especially for Al, Ca, Mg, Si and Zn. Otherwise are the results quite in accordance with L/S 2 and L/S 10 in the column test and L/S 50 in the serial batch test. On the other hand are the Cr-figures in the modified DIN test quite the same, in contrast to the column test.

Table 18
Modified DIN test of 6B

	LS 2	LS 10	LS 50	pH 4
	ppm	ppm	ppm	ppm
Al	<0,022	0,14	1,9	95
B	<0,025	<0,025	<0,025	<0,025
Ba	0,20	0,031	<0,004	0,27
Ca	700	290	29	2100
Co	<0,005	<0,005	<0,005	0,048
Cr	0,062	0,017	<0,010	0,11
Cu	<0,004	<0,004	<0,004	1,3
Fe	<0,005	<0,005	<0,005	63
K	3780	210	7	34
Li	0,40	0,14	0,017	0,57
Mg	<0,027	0,35	0,11	93
Mn	<0,002	<0,002	<0,002	10,2
Mo	0,20	0,020	<0,006	<0,006
Na	620	35	0,9	13
Ni	0,026	<0,019	<0,019	0,098
P	<0,090	<0,090	<0,090	11,3
Pb	<0,040	<0,040	<0,040	1,3
Si	16	14	3	124
Sr	5	0,90	0,064	15
V	<0,007	0,022	0,011	0,12
Zn	<0,002	<0,002	<0,002	0,73

Ag, As, Be, Cd, Hg, Sb, Se, Sn, Ti, and Tl was below the detection limit in alle the leachates.

The results of sample 6B in table 18 is also comparable with the earlier leaching tests, as it was for sample D147 and D148.

2.3.4 DIN 38414 S4

In the DIN test 100 grams of crushed sample (<10 mm) is added 1000 ml demineralized water and agitated for 24 hours. The solution is then filtered, pH and conductivity is measured, and the solution is conserved and analysed. The results are listed in table 19. The DIN test was originally developed for testing of sludges (19).

Table 19
DIN 38414 S4 test of all samples

	D147	D148	6B	7/5	19/5	22/5
	ppm	ppm	ppm	ppm	ppm	ppm
Al	0,29	0,28	1,1	<0,022	0,035	<0,022
Ba	0,51	0,51	0,070	0,45	0,44	0,38
Ca	820	810	410	1030	1030	1050
Co	0,010	0,007	<0,005	<0,005	<0,005	<0,005
Cr	0,016	0,030	0,014	1,4	1,8	2
Cu	<0,004	<0,004	0,007	<0,004	<0,004	<0,004
Fe	0,011	0,015	<0,005	<0,005	<0,005	<0,005
K	16	150	590	680	670	720
Li	0,19	0,18	0,14	0,30	0,29	0,33
Mg	<0,027	<0,027	0,12	<0,027	0,034	<0,027
Mo	<0,006	<0,006	0,035	0,092	0,10	0,10
Na	55	55	110	140	140	165
Si	0,26	0,29	9	0,26	0,29	0,26
Sr	4,3	4,1	1,4	3,6	3,1	3,1
V	<0,007	<0,007	0,018	<0,007	<0,007	<0,007
pH	11,9	11,7	10,4	11,6	11,5	11,6
C mS/cm	8,2	8,4	3,5	12,6	10,4	11

Ag, As, B, Be, Cd, Hg, Mn, Ni, P, Pb, Sb, Se, Sn, Ti, Tl and Zn was below the detection limit in alle the leachates in the DIN test.

If the results of the German DIN test is compared with the modified DIN test (at L/S 10) it is quite obvious that there is an effect of the initial acidification in the modified DIN test. In the German DIN test pure water is used.

2.3.5 Toxicity Characteristic Leaching Procedure

In the Toxicity Characteristic Leaching Procedure test 100 grams of crushed sample (<9,5 mm) is added 2000 ml acidified (to pH 2.88 with 5.7 ml glacial acetic acid/litre) demineralized water and rotated for 18 hours. The solution is filtered, pH and conductivity is measured, and the solution is conserved and analysed. The results are listed in table 20. The Toxicity Characteristic Leaching Procedure test is originally developed for testing leaching in a mixed landfill (20).

Table 20
EPA TCLP test of all samples

	D147	D148	5/5	19/5	22/5	6B
	ppm	ppm	ppm	ppm	ppm	ppm
Al	0,17	0,34	0,026	0,028	0,022	0,14
B	0,076	0,037	<0,025	<0,025	<0,025	0,032
Ba	0,29	0,32	0,60	0,63	0,58	0,12
Ca	2120	2140	2300	2470	2460	2290
Co	<0,005	0,007	<0,005	<0,005	<0,005	0,016
Cr	0,15	0,29	0,95	1,29	1,46	<0,010
Cu	<0,004	<0,004	<0,004	<0,004	<0,004	0,047
Fe	<0,005	0,007	<0,005	<0,005	<0,005	0,020
K	76	78	360	360	390	330
Li	0,25	0,25	0,28	0,28	0,31	0,25
Mg	0,77	0,23	0,10	0,041	0,061	18
Mn	<0,002	<0,002	<0,002	<0,002	<0,002	1,5
Mo	<0,006	<0,006	0,038	0,058	0,054	0,011
Na	30	30	70	80	95	55
Si	14	8	1,3	0,64	0,83	14
Sr	4,2	3,9	4,0	3,8	3,5	3,0
V	0,020	0,009	<0,007	<0,007	<0,007	0,009
pH	11,6	11,9	12,5	12,8	12,7	7,2
C mS/cm	5,8	5,8	6,5	8,7	7,6	7

Ag, As, Be, Cd, Hg, Mn, Ni, P, Pb, Sb, Se, Sn, Ti, Tl and Zn was below the detection limit in alle the leachates.

In the TCLP test there is obvious an pH effect of the more stronger acidification than in the L/S 20 of the serial batch test, but this has no measurable dramatic effects with regards to leaching of heavy metals from this type of samples.

4 CONCLUSION

This study has so far shown that waste fuel used as supplementary fuel in the production of cement is enriched with regards to heavy metals. The heavy metals are to a high extent retained in the clinker but the dilution factor in the process is great. The additional content of heavy metals in clinker caused by the waste fuel is small for most elements and not measurable for some. Performance of different leaching tests has shown that the leachability are quite the same in all the samples, regardless if its produced with waste as fuel or not. The results from the different tests seems to be in accordance, but it will be performed additional analysis with more sensitive techniques to confirm this also for the trace elements.

ACKNOWLEDGEMENT

I gratefully thanks The Norwegian Research Council and Norcem FoU Brevik which have financed the project and Ingegerd Rustad at SINTEF SI which have performed the chemical analyses.

REFERENCES

- 1) Ahling, B., Destruction of chlorinated Hydrocarbons in a Cement Kiln, *Environmental Scientific Technology*, 13 (1979) 1377.
- 2) lee, C.C., Huffman, G.L. and Oberacker, D.A., An overview of hazardous toxic waste incineration, *JAPCA*, 36 (1986) 922.
- 3) Oppelt, E.T., Incineration of hazardous waste - A critical review, *JAPCA*, 37 (1987) 558.
- 4) Benestad, C., Incineration of hazardous waste in cement kilns, *Waste Management & Research*, 7 (1989) 351.
- 5) Karstensen, K.H. and Benestad, C., Burning of hazardous wastes as co-fuel in a cement kiln - Norwegian experiences. Conference proceedings of Kilnburn'92, September 10-11, Brisbane, 1992.
- 6) Mantus, E.K., All fired up - Burning hazardous waste in cement kilns. Report from Environmental Toxicology International Inc. & The Combustion Research Institute, Seattle, 1992.
- 7) Slood van der, H.A., Systematic leaching behaviour of trace elements from construction materials and waste materials, *Waste materials in construction, Studies in environmental science* 48, Elsevier, Amsterdam, 1991.
- 8) Slood van der, H.A., Hoede, D. and Bonouvie, P., Comparison of different regulatory leaching test procedures for waste materials and construction materials. Report ECN-C-91-082, Petten, 1991.
- 9) Rankers, R.H. and Hohberg, I., leaching tests for concrete containing fly ash - evaluation and mechanism. *Waste materials in construction, Studies in environmental science* 48, Elsevier, Amsterdam, 1991.
- 10) Rechenberg, W., Sprung, S. and Sylla, H.M., A test method for the determination of leachability of trace elements from wastes bound with cement. *Waste materials in construction, Studies in environmental science* 48, Elsevier, Amsterdam, 1991.

- 11) Branscome, M. and Mournighan, R.E., Hazardous waste combustion in industrial processes - Cement and lime kilns. Report EPA 600/2-87-095, Cincinnati, 1987.
- 12) Sprung, S., Technological problems in pyroprocessing cement clinker - cause and solution. Beton - Verlag GmbH, Dusseldorf, 1985.
- 13) Seebach von, M. and Gossman, D., Cement kilns - sources of chlorides. Conference proceedings of AWMA conference on waste combustion in Boilers and industrial furnaces, April 18-20, Kansas City, 1990.
- 14) Karstensen, K.H. and Lund, W., Multielement analysis of MSWI reference sample - BCR 176, Journal of Analytical Atomic Spectrometry, 4 (1989) 357.
- 15) European Standard EN 196 Part 1, Methods of testing cement - Determination of strength, May 1987.
- 16) Karstensen, K.H. and Lund, W., Multielement analysis of city waste incineration ash and slag by ICP-AES, The Science of the Total Environment, 79 (1989) 179.
- 17) NVN 5432 Dutch pre-standard. Determination of the maximum leachable quantity and the emission of potentially hazardous components from construction materials, monolithic waste materials and stabilised waste products of mainly inorganic character. May, 1991.
- 18) NVN 2508 Dutch pre-standard. Determination of leaching characteristics of coal combustion wastes. February, 1988.
- 19) DIN 38414 S4 German standard procedure for water, wastewater and sediment testing - sludge and sediment. Determination of leachability. Institut fur Normung, Berlin, 1984.
- 20) Toxicity Characteristic Leaching Procedure. Federal Register No 261, March 29, 1990.



本文献由“学霸图书馆-文献云下载”收集自网络，仅供学习交流使用。

学霸图书馆（www.xuebalib.com）是一个“整合众多图书馆数据库资源，提供一站式文献检索和下载服务”的24小时在线不限IP图书馆。

图书馆致力于便利、促进学习与科研，提供最强文献下载服务。

图书馆导航：

[图书馆首页](#) [文献云下载](#) [图书馆入口](#) [外文数据库大全](#) [疑难文献辅助工具](#)