Project BioCrete **Task ID: 5**

Final report

Environmental impact of bio-ash concrete

Performed by:
Jorn Bodker

Taastrup, October, 2007

Byggeri

Title: Environmental impact

Authors: Jorn Bodker

Content

1. Preface

“BioCrete” is the acronym for a LIFE supported project ”Utilisation of ash from incineration of wastewater sludge (bio ash) in concrete production”. The project activities have been defined in 10 tasks, and the present report is the final report of task 5, summarising purpose, task progress, results and experiences.

The project period is June 2005 to December 2007, and the project includes 4 participants: Avedoere Wastewater Services (AWS) as beneficiary, Lynettefaellesskabet (LYNIS) and Unicon Ltd. (UNICON) as partners and Danish Technological Institute (DTI) as consultant.

2. Background

Ash from incineration of wastewater sludge (bio ash) has not previously been used in concrete on a regular basis. In order for bio ash to be an accepted raw material for concrete production it must be documented that concrete containing bio ash does not leach heavy metals in large amounts compared to the leaching of heavy metals from ordinary concrete not containing bio ash.

The leaching of heavy metals takes place from the concrete while the constructions are still in use, but more important is the fact that the leaching takes place at the end of the life cycle, when the concrete is crushed and probably used as filling material in road construction.

In order to investigate the leaching potential from the concrete in the two life cycle stages, leaching tests have been carried out on a monolithic sample of concrete (10 x 10 x 10 cm cube) and on samples of crushed concrete.

In the last life cycle stage the concrete is carbonated (carbon dioxide from the atmosphere is absorbed in the concrete). This situation is simulated in the tests, and before the leaching test performed in the laboratory, the sample of crushed concrete was exposed to carbon dioxide until fully carbonated.

3. Methods

3.1 Analysis of the raw materials

Samples of bio ash, fly ash and cement are analysed for the content of heavy metals.

The analysis of powder materials is carried out at the Danish Technological Institute according to the method UT012 which is equivalent to Danish Standard method DS 259. The samples are dissolved in semi-concentrated nitric acid at 120 ˚C in 30 minutes followed by an analysis on ICP-AES.

3.2 Crushed samples

Samples of concrete containing bio ash and samples of concrete not containing bio ash have been crushed to a particle size less than 4 mm.
The crushed samples are divided into two samples. One sample of concrete is stored in an airtight container until the leaching tests can take place. The other sample is stored in pure CO_2 for 1-2 months until it is totally carbonated.
The carbonation takes some time and especially the concrete with low w/c-ratio may not be completely carbonated after two months

The carbonation takes place in an desiccator at a relative humidity of 56%. The humidity is controlled by a saturated solution of magnesium nitrate in water.

Both carbonated and not carbonated samples of concrete have been put through the batch leaching test CEN prEN 12457-3 with a liquid to solid ratio L/S of 2 l/kg. The liquid is demineralised water. This method is described in the Danish government order on utilization of residues and soil for construction works no. 1635 from 13/12/2006.
The test has been carried out at the laboratory at the Danish Technological Institute, and parallel tests have been carried out by Aalborg Portland.

The concentration of metals in the leaching test is measured by ICP-MS (Inductively Coupled Plasma Mass Spectrometry) or ICP-AES (Inductively coupled plasma optical emission spectroscopy). All the measurements carried out by Aalborg Portland is by ICP-AES while the Danish Technological Institute has used ICP-MS for one part of the elements and ICP-AES for the rest of the elements.
These methods do not distinguish between chromium in the two stages of oxidation Cr +3 and Cr +6.

3.3 Monolithic samples

In order to investigate the leaching of heavy metals from concrete in the life cycle phase where the concrete is still part of an undamaged construction, a couple of tank test on concrete cubes have been carried out.

Cubes of 10 x 10 x10 cm are cast in the laboratory, and after a curing time of approx. 3 months the leaching from the samples are tested according to the Dutch method NEN 7345. The test is carried out by the Energy Research Centre of the Netherlands.

4. Results

4.1 Composition of concrete

In the laboratory at the Danish Technological Institute a number of concrete samples to be tested for leachability was cast, and in the table below the composition of the concrete samples is listed.

	Reference concrete P20	**Bioash concrete**
Cement	201.6	211.6
Fly ash from coal fired power plant	59.9	34.5
Bio ash		34.6
Water	155	162.7
Aggregate, fine	847.1	829.7
Aggregate, coarse	974.1	954.1

Table 1. Composition of an ordinary reference concrete and of a concrete with bio ash. The concrete is made in exposure class "passive" and the composition is in kg/m^3

	Reference concrete A35	**Bioash concrete**
Cement	323.8	336.3
Fly ash from coal fired power plant	64.9	37
Bio ash		37.1
Water	149.5	155.2
Aggregate, fine	778	751.5
Aggregate, coarse	970.8	951.2

Table 2. Composition of an ordinary reference concrete and of a concrete with bio ash. The concrete is made in exposure class "aggressive"and the composition is in kg/m^3

At the wastewater plant of Avedore two types of bio ash are generated; an ordinary red coloured ash on the basis of iron as a precipitating agent and a more pale coloured ash on the

basis of aluminium as a precipitation agent. The pale bioash is made of sludge from the treatment plant Damhusaaen. The sludge from treatment plant Damhusaaen has been taken to the incineration plant in Avedoere and incinerated there.
Samples of concrete containing both types of ash have been cast and tested.

4.2 Composition of the constituents of concrete samples

The various bio ashes, fly ash from a coal fired power plant and cement which has been used for casting of the concrete samples are analysed for the content of heavy metals.

Metal	"White" bio ash (AWS2) 06/08/21	Ordinary bio ash from AWS (AWS 3) 06/06/19	Bio ash from LY-NIS (LYNIS1) 06/07/26	Fly ash from Hammer-holmen 07/01/16 Avedøre-værket blok 1	Aalborg Portland RAPID Cement Batch 160207
As	10.9	12.5	3.5	19	8.8
Ba	590	960	770	1020	340
Bi	6.5	9	5.4	1.3	0.38
Cd	2.8	5.4	2.5	1.53	0.69
Cr	37	64	44	54	21
Cu	440	790	620	43	46
Hg	7.2	11	n.a.	0.34	0.05
Mn	490	680	500	280	131
Mo	16	21	14	16	1.7
Ni	47	62	41	33	20
Pb	180	170	170	24	16
Sb	6.1	10.9	6.3	0.96	n.a.
Se	18.4	13.3	n.a.	5.5	0.96
Tl	0.9	0.88	0.38	0.7	n.a.
V	32	30	35	153	55
Zn	1500	1800	2300	60	136

Table 3. Composition of ashes and cement in mg/kg. N.a. is not analyzed.

4.3 Leaching from crushed samples of concrete

4.3.1 Tests carried out by the Danish Technological Institute

In the table below the composition of leachate in the test of concrete made in passive exposure class – P20 – is listed.

Pas-sive	Bio ash Lynis 1		Bio ash AWS 3 (Standard)		Bio ash AWS 2 (White)		Reference con-crete	
	No car-bona-tion	Full car-bona-tion	No car-bona-tion	Full car-bona-tion	No car-bona-tion	Full car-bona-tion	No car-bona-tion	Full car-bona-tion
Ag	<2	<2	<2	<2	<2	<2	<2	<2
As	<2	<2	<2	<2	<2	<2	<2	2,8
Ba	2850	50	3100	55	2500	48	3420	50
Bi	<2	<2	<2	<2	<2	<2	<2	<2
Cd	<2	<2	<2	<2	<2	<2	<2	<2
Cr	27	340	16.6	20.1	32.7	78	26	130
Cu	7.6	3.6	6.1	5.3	6.4	4.3	6.3	5
Hg	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Mn	<2	<2	<2	19	<2	3.5	<2	<2
Ni	6.4	2.3	-	5	-	4.9	8.9	2.1
Pb	<2	<2	1.64	<2	1.89	<2	<2	<2
Sb	<2	4.2	<2	3.14	<2	3.35	<2	2.9
Se	2.2	15	4.2	26	4	27	2.3	17
Sn	<2	<2	<2	<2	<2	<2	<2	<2
TI	<2	<2	<2	<2	<2	<2	<2	<2
V	<2	93	<2	13.7	<2	14	<2	61
Zn	3.9	<2	<2	<2	<2	<2	4	<2
Mo	11	150	13.6	180	12.6	130	9.6	160
pH	11.2	9	11.7	7.3	11.4	6.9	11.7	9

Table 4. Composition of leachate from tests of concrete made in exposure class "passive". The concentrations are given in µg/litre. "<" means below limit of detection.

Also concrete made in aggressive exposure class A35 was tested, and in the table below the composition of leachate in the test of concrete made in aggressive exposure class is listed.

Ag-gres-sive	**Bio ash Lynis 1**		**Bio ash AWS 3 (Standard)**		**Bio ash AWS 2 (White)**		**Reference con-crete**	
	No car-bona-tion	**Full car-bona-tion**	**No car-bona-tion**	**Full car-bona-tion**	**No car-bona-tion**	**Full car-bona-tion**	**No car-bona-tion**	**Full car-bona-tion**
Ag	<2	<2	<2	<2	<2	<2	<2	<2
As	<2	2,2	<2	2	<2	<2	<2	<2
Ba	3100	<25	2370	50	1730	32	2200	49
Bi	<2	<2	<2	<2	<2	<2	<2	<2
Cd	<2	<2	<2	<2	<2	<2	<2	<2
Cr	2.9	16.1	20.8	75	20.2	45	24.4	86
Cu	7.7	3.5	14	4.7	11.2	5.6	12	4.9
Hg	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Mn	<2	3.5	<2	4.3	<2	4.9	<2	5.7
Ni	3	0.9	1.7	2.9	<2	3.7	2.15	3.3
Pb	<2	<2	2.33	<2	2.39	<2	2.01	<2
Sb	<2	2.51	<2	5.1	<2	3.28	<2	6
Se	2.2	15	3.7	16	4	19	3.9	15
Sn	<2	<2	<2	<2	<2	<2	<2	<2
TI	<2	<2	<2	<2	<2	<2	0.5	<2
V	<2	24.7	<2	17.7	<2	17.1	<2	12.9
Zn	4.1	<2	<2	<2	<2	<2	<2	<2
Mo	6.4	88	8.6	92	9.2	96	8.4	91
pH	11.8	7.5	11.3	7.3	11.3	7.1	11.2	7

Table 5. Compostion of leachate from tests of concrete made in exposure class "aggressive". The concentrations are given in µg/litre "<" means below limit of detection.

4.3.2 Tests carried out by Aalborg Portland

In the table below the composition of leachate in the tests carried out by Aalborg Portland is listed.

Aggres-sive	Bio ash AWS 3 (Standard)		No bio ash	
	No carbonation	Full carbonation	No carbona-tion	Full carbona-tion
Sb	< 45	< 45	< 45	< 45
As	< 80	< 80	< 80	< 80
Cd	< 2	< 2	< 2	< 2
Cr	< 100	111	< 100	110
Co	< 4	< 4	< 4	< 4
Cu	12	10	9	9
Pb	< 30	< 30	< 30	< 30
Mn	< 5	< 5	< 5	< 5
Ni	< 7	< 7	< 7	< 7
Tl	< 30	< 30	< 30	< 30
V	6	126	6	144
Zn	< 10	< 10	< 10	30
S	1867	207272	1222	165196
pH value	12.61	10.1	12.68	10.3
Conductivity in µS/cm	9640	1413	9880	1184

Table 6. Composition of leachate from tests of concrete made in environmental class "aggressive". The concentrations are given in µg/litre "<" means below limit of detection.

4.4 Leaching from monolithic concrete sample

In the table below the total emission from the monolithic sample of concrete is listed. The emission is measured from three different samples, and on this basis the total emission after 64 days are calculated.

The test is carried out on two samples of concrete in passive environmental calls. The concrete with bio ash no 3 from AWS and a reference concrete with no bio ash are tested. Both samples have been stored in plastic bags until testing, and the samples have not been exposed to carbon dioxide.

	Bio ash AWS 3 (Standard)	No bio ash
As	0.81	1.42
Ba	4.91	0.59
Cd	0.43	0.43
Cr	3.05	0.94
Cu	0.3	0.33
Mo	0.71	0.87
Ni	0.48	0.63
Pb	0.25	0.67
S	738.9	433.5
Sb	1.11	1.01
Se	1.72	3.03
Sn	0.82	1.01
SO4	2048	1210
V	10.7	6.25
W	0.4	0.37
Zn	0.98	1.16

Table 7. Emission of heavy metals and various ions from monolithic samples of concrete. Calculated emission in 64 days. Values are in mg/m^2.

5. Discussion

5.1 Heavy metals in the bio ash

Samples of bio ash, fly ash and cement have been analysed for heavy metals. Several metals are found in elevated concentration in the bioash compared to the fly ash and cement.

5.2 Release of heavy metals from crushed concrete

The concentration of metal in the leachate can be compared to the threshold limit values in the ministerial order from the Danish EPA no 1635 of 13/12/2006 on the recycle of residues and soil for construction works.

It must be emphasized that the ministerial order no 1635 of 13/12/2006 does not regulate the issue of crushed concrete, as well as the ministerial order does not say anything about carbonation of concrete. However, the regulation gives a set of concentrations of heavy metals in leachate that soil and other kinds of residues must meet, if used for construction works.

In the table below the threshold limit values for the various heavy metals in leachate found in the ministerial order no 1635 from the Danish EPA is listed.

	Category 1	**Category 2**	**Category 3**
As	8	8	50
Ba	300	300	4000
Cd	2	2	40
Cr	10	10	500
Cu	45	45	2000
Hg	0.1	0.1	1
Mn	150	150	1000
Ni	10	10	70
Pb	10	10	100
Zn	100	100	1500

Table 8. Limit values of heavy metals in leachate. Concentrations are in µg/litre.

None of the concrete samples tested in the batch leaching test CEN prEN 12457 results in concentrations in the leachate exceeding the limit values of category 3 in the DEPA-ministerial order no 1635.

The limit value of barium in category 2 is exceeded by leachate from all types of concrete which have not been exposed to carbon dioxide. After exposure to carbon dioxide the concentration of barium in the leachate drops below the limit value of category 2.

Almost all types of concrete tested releases relatively large amounts of chromium. The concentration of chromium in the leachate from not CO_2-exposed concrete exceeds the limit value of category 2. After carbonation of the concrete the release of chromium accelerates.

As it is the case for chromium, the release of some metals is accelerated by the carbonation while, as it is the case for barium, the release of other metals is reduced by the carbonation.

5.3 Leaching from a monolithic sample of concrete

The release of various ions in the test carried out on a monolithic sample of concrete can be compared to the Dutch "building material decree".

	Category 1	Category 2	Bio ash AWS 3	No bio ash
As	41	140	0.81	1.42
Ba	600	2000	4.91	0.59
Br	29	95	n.a.	n.a.
Cd	1.1	3.8	0.43	0.43
Cl	18000	54000	n.a.	n.a.
Co	29	95	n.a.	n.a.
Cr	140	480	3.05	0.94
Cu	51	170	0.3	0.33
F	1300	4400	n.a.	n.a.
Hg	0.43	1.4	n.a.	n.a.
Mo	14	48	0.71	0.87
Ni	50	170	0.48	0.63
Pb	120	400	0.25	0.67
S	107000	320000	738.9	433.5
Sb	3.7	12	1.11	1.01
Se	1.4	4.8	1.72	3.03
Sn	29	95	0.82	1.01
SO4			2048	1210
V	230	760	10.7	6.25
W	no limit	no limit	0.4	0.37
Zn	200	670	0.98	1.16

Table 11. Dutch building material decree compared to the results from the actual test. The values are in mg/m2/64 days.

The emission of all the metal ions from the two tested samples of concrete is, except for selenium, below even Category 1 in the Dutch building material decree.
The Dutch laboratory who has carried out the tests has informed that the values for the release of selenium is very close to the limit of detection, and that the values may be overestimated.

6. Summary and conclusion

The environmental impact of bio ash concrete is evaluated using a method of characterization (defining 3 categories of residues) described in the Danish ministerial order No. 1635 of 13. December 2006 “Recycling of residues and soil for construction works” and comparing with a similar characterization of a reference concrete with no bio ash.

Thus, according to the ministerial order, the present characterization is based upon a European leaching test method prEN 12457-3 (June 1998), and the leachate has been analyzed for 19 heavy metals: Ag, <u>As</u>, <u>Ba</u>, Bi, <u>Cd</u>, Co, <u>Cr</u>, <u>Cu</u>, <u>Hg</u>, <u>Mn</u>, Mo, <u>Ni</u>, <u>Pb</u>, Sb, Se, Sn, Tl, V, <u>Zn</u>, and in the ministerial Order the underlined 10 metals are attributed with leachate limit values which define residue category.

Further, in order to simulate behaviour of fresh (i.e. not carbonated) as well as aged (i.e. carbonated) concrete, the concrete samples have been tested after no exposure to carbon dioxide as well as after 1 – 2 months of exposure to carbon dioxide.

In this way 6 different bio ash concrete samples have been tested, and in total 20 leachates have been analyzed.

Comparison between bio ash concrete and reference concrete: For all heavy metals and for not carbonated as well as carbonated concrete samples there is no significant difference between the concentrations in the bio ash concrete leachate and the reference concrete leachate. This is the case although the concentration of some heavy metals (Bi, Cu, Hg, Pb, Se and Zn) is approximately ten times higher in bio ash as in cement and as in fly ash.

Category characterization (category 1 is the best): No metal exceeds category 3. Chromium (Cr) corresponds to category 3. Barium (Ba) also corresponds to category 3 if the concrete sample is not carbonated, but to category 1 when carbonated. Mercury (Hg) probably corresponds to category 1, but the analytical detection limit was too high in order to be sure. The remainder 7 metals correspond to category 1.

Thus, because of chromium (and barium) the bio ash concrete corresponds to a category 3 residue – but the same is the case for the reference concrete!

Two leaching tests (bio ash + reference) according to a Dutch Standard method show leachate heavy metal concentrations far below the category 1 limit values.

The overall conclusion is that the use of bio ash for concrete production has very limited environmental impact.