A Leverantörens processbeskrivning

A NEW STABILIZATION PROCESS FOR THE FLYASH AND THE WASTE WATER TREATMENT SLUDGES FROM WASTE TO ENERGY PLANTS

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ABSTRACT.

In Europe, MSW incineration fly ash disposal calls for physico-chemical tests and in order to be able to dispose of the ash at a reasonable cost, some stabilization of the fly ash is needed. Also, when a wet scrubber is used for flue gas cleaning, the waste water treatment generates a sludge or a cake rich in heavy metals that must also be disposed of. In order to meet the growing pressure for only one solid stream to be dealt with, a process that stabilizes the mixture of fly ash and the sludge produced by the waste water treatment has been developed. This paper describes the process used and shows that not only the compulsory tests for heavy metals leaching and percolation are met, but also that the eco-toxicity, as described by the "H14"is much reduced and classify the residues as "non toxic for the environment". Actual plant data presenting leaching, percolation and ecotoxicity test results is given.

Key words: MSW INCINERATION FLY ASH SLUDGES WATER TREATMENT ECOTOXICITY WASTE ENERGY

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INTRODUCTION

In 2005, waste to energy represents 59 million tons per year in Europe (CEWEP, Eurostat). Among the different options (incineration, recycling, composting, landfilling) municipal waste incineration is a solution that allows up to 90% volume reduction of ultimate waste and recovers energy, and therefore is a form of recycling. While it is by no mean the answer to all waste problems, waste to energy can recover renewable and sustainable energy from a waste, and can be a source of electricity or district heating in many cases. This incineration process, while producing energy also yields solid wastes like the bottom ash and fly ash. The fly ash is considered toxic and must be disposed of with care. In many cases, a wet scrubbing option is selected for the flue gas train, and in such case the plant includes a waste water treatment unit that will remove the heavy metals from the waste water, but that will produce a sludge or a cake that contains most of the heavy metals. In many cases, this cake, resulting from the dehydratation of the waste water treatment sludge is separately disposed of, but this represents an additional burden for the plant since two solids waste streams must be eliminated. It has been proposed to blend the fly ash and the sludge from the waste water treatment into a single stream of humid solids. Much work has been done that focuses on the behaviour of the heavy metals, mostly using leaching or percolation tests, because such tests are mandatory, in order to determine how the waste can be actually disposed. But only a limited amount of research has been made in terms of the real ecotoxicity of such waste.

PROTOCOLS, EQUIPMENT AND METHODS

Solids sampling

Chemical composition and physical characteristics of the treated ash produced by the detoxification process are directly linked to the composition of what has been incinerated, and this is much dependant on the season, but also varies on a daily basis. In France the average composition of the waste is as shown in Figure 1 (EIONET).

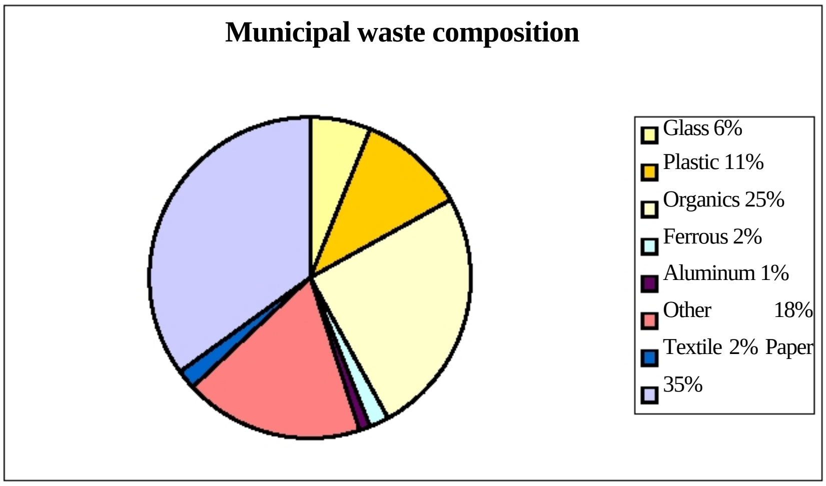

Figure 1

Work has been done on a Municipal Waste Incineration plant that uses a wet scrubbing system, located in the Northern part of Europe. The samples have been taken after a stable period of operation of more than 12 hours. Each sample has been taken by taking several sub samples at the outlet of the band filter, until a total of about 10 kilograms have been collected. The 10 kilo samples have been thoroughly mixed and sent to the external laboratory that performed the leaching tests, the percolation test and the excotoxicity tests. The entire procedure has been repeated for several days.

Leaching tests

The leaching tests have been performed as per EN 12457-2 (reference EN 12457-2 (2002), X30-402-2). For such tests, a quantity of about 90 grams of dry matter is contacted by shaking for 24 hours with ten times the amount of pure water. The dry matter is determined as per EN 14346. The suspension is then filtrated, and the clear filtrate is analyzed for heavy metals, chlorides, sulfates. The results are expressed as mg of metals per kilo of dry solids. The allowable limits are given in Table 1.

Percolation tests

The percolation tests were conducted in an external laboratory, using EN 14405. In this method, a continuous up flow of water is recirculated across a static bed of the solids to be tested. Eventually the water is saturated with the pollutants to be tested and is analyzed. This enables a conclusion to be drawn from the results as which components are rapidly being washed out and which components are released under the interactions in the matrix. The length of the column is 30 cm, the slip velocity is 15 cm/day and the duration of the test is 30 days, at liquid to solid ratio of 10:1. Again the results are expressed as mg of pollutant per kilo of dry solid. The allowable limits are given in Table 1.

Heavy metals, chlorides, sulfates

The leachates were obtained using the leaching protocol EN 14257. The soluble fraction is given as the ratio of the cumulative weight of each dry residues (of the 3 leachates) divided by the dry weight of the sample used. This soluble fraction is mostly made of NaCl, KCl, $CaCl_2$ and $CaSO_4$.

The heavy metals (Cd, Pb, Hg) are obtained by atomic absorption spectrometry (AAS) using a Unicam 969 with Solaar software. Confidence interval is around 5% and detection limit is 1ppb.. Sulfates (SO_{4--}) was determined by gravimetric method using barium sulfate precipitation (reference NFT 90.009). Chlorides was determined using manual titration with mercury nitrate (reference AMINOT A. (1974))
Several calibration solutions were made from known solutions

Ecotoxicity testings

For waste from incineration plants, European community council (ECC) has set 14 properties that would classify the waste as dangerous, including the ecotoxic hazard, criteria H14 (reference European directive 91/689, 1991). The MEDD (Ministère de l'écologie et du développement durable) has proposed a method in 1998 and 2000 that requires two different approaches that complement each other: A direct approach, working on the solids themselves and an indirect approach based on leachates from the solids. In April 2000 (reference April 2000, MEDD) MEDD has issued provisional limits stating that a solid waste would be labeled as ecotoxic when: (1) the leachate, when diluted more than one hundred times, would inhibit by more than 20% the reproduction of Ceriodaphnia dubia, or (2) the solid waste, when diluted more than 10 times in the substrate, would inhibit sprouting or growth of lettuce by more than 50%.

1. *Ecotoxicity testings performed on leachates*

The leachates have been obtained using the EN 12457-2 (2002) protocol, with a liquid to solids ratio of 10. The leachate have been pH adjusted to 8.5 using 70% nitric acid, and filtered on a 0.45 m filter.

Daphnia test

This is an acute toxicity test. The immobilisation test on Daphnia Magna of May 1996 (reference AFNOR NF EN ISO 6341: 1996) is used. This test is based on the determination of the concentration that freezes 50% of the daphnia after 24 or 48 hours. This concentration is called the $CI_{50\%}$ concentration. The protocol involves two steps: a preliminary test yielding an estimate of $CI_{50\%}$ in 24 hours serves the purpose of narrowing the concentration range used for the final test; and a final test conducted by selecting a range of concentrations, usually in geometric progression, so as to bracket the initial range that during the preliminary test yielded 0% and 100% freeze percentage.

Death test on Ceriodaphnia

This is a chronic toxicity test. AFNOR protocol is used (reference AFNOR NF T90-376: 2000), except that Evian water rather than the M4 medium has been used. Young ceriodaphnias of age between 6 and 24 hours are exposed to several dilutions of the leachate for 7 days, the leachate being removed. The death rate of the females and the number of youngsters produced are counted daily. We note as CE_x% the death rate, as a function of percentage of leachate used after 7 days, with reference to a blank.

Fluorescence inhibition of marine bacteria

This is the MICROTOX or Vibria Fischeri test, (ISO 11348-3: 1998), another acute toxicity test. The concentration on the lixiviate that after 5, 15, and 30 minutes inhibits 50% of the emitted light of the bacteria is obtained. This concentration is called the CE_{50-t}, t being the contact time of the bacteria and the used dilation.

Inhibition of algae growth

The chronic toxicity test is used (NF T 90-375: 1998), with Pseudokirchneriella subcapitata, formerly Selenastrum capricornutum. The eluate concentration that inhibits the growth by 20% is called the CE 20%. Each dilution is done six times.

2. Ecotoxicity tests performed on selected samples of solids.

Inhibition of seed germination by a contamination soil

Bottom ash are diluted in the ISO soil (ISO 11269-2: 1995). Different seeds (lettuce, barley) are planted in pre-set soils containing the diluted solids. Three repetitions are made. The test has two steps: a 7 day preliminary test with concentrations corresponding to no dilutions and 100:1 dilution, followed by a final test using 5 dilutions, bracketing the dilutions factors for which germination raise from 0 to 100% in the preliminary test. After 14 days the biomass in each pot is measured by weighing.

Mortality of worms (Eisenia Fetida)

This is the test (ISO11268-1: 1994) quite similar to the previous one, with also two steps. Ten worms are introduced in the diluted solid to be tested, and a count of the living worms is done after 7 and 14 days.

DESCRIPTION OF THE PROCESS

A wet scrubbing system usually comprises the following and can be simplified as shown on figure 2.

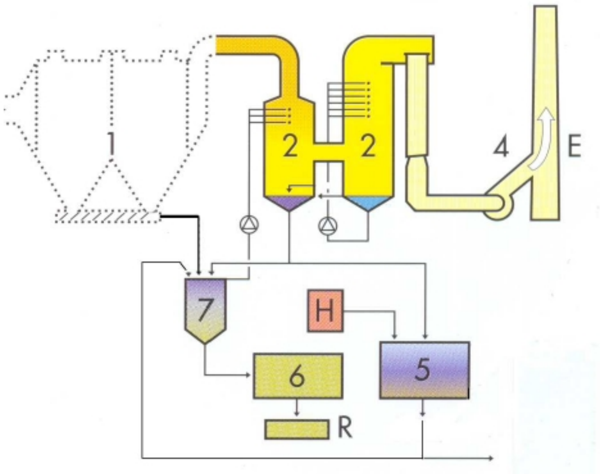

Figure 2: Wet Scrubbing process diagram

The off gases emitted by the incinerator are first admitted to an electrostatic precipitator (1) (ESP). The gases, free from most of the dust, then enter two scrubbers (2), an acidic wet scrubber, where the pH is kept under 2.5 and a neutral scrubber where the pH is maintained above 5. The bleed from the scrubbers would normally go to a waste water treatment (5) where some additional reagents, like sodium hydroxide, calcium hydroxide, flocculating and chelating agents are added. The main output of the waste water treatment is a stream of clear, metal free water that can be safely released to the environment. The heavy metals, precipitated in the waste water treatment form a sludge that is usually dehydrated in a press filter, so as to yield a cake (R) that will be discharged. In the process that has been developed, instead of dewatering the sludge from the waste water treatment (5) it is mixed with the fly ash coming from the precipitator (1). Some water is added, and some of the acidic liquors from the scrubber (2) is added in a stirred tank (7). The heavy metals already precipitated and chelated in the waste water treatment bind to the fly ash, and at the same time the soluble fraction of the fly ash, mostly comprised of sulfates, chlorides, calcium and sodium, is dissolved, and will end in the clear water stream out of the waste water treatment. The sludge that is formed in the stirred tank (7) goes to a band filter (6).

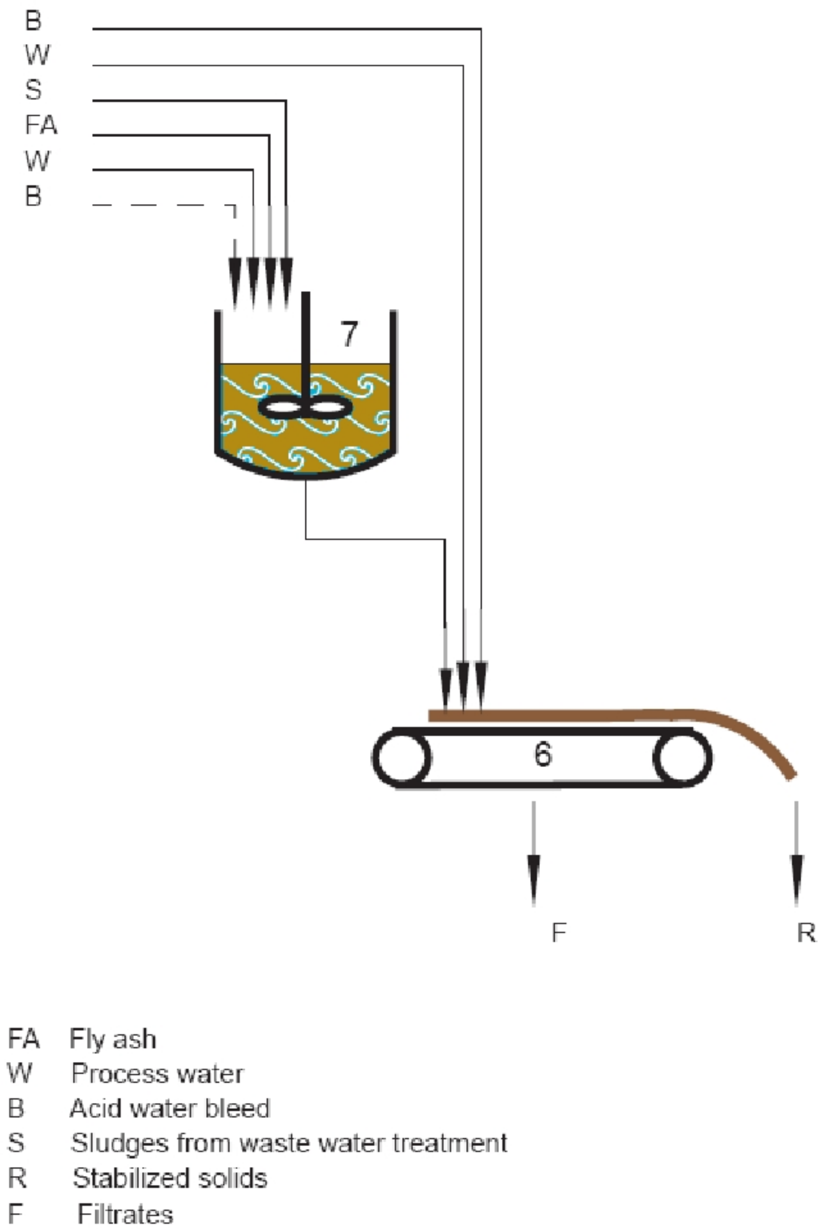

Figure 3: general overview of the TIIL process

As already indicated, the sludge and the fly ash are contacted with water and acidic liquors, and the resulting mixture is fed to a band filter (6). On this band filter, rinsing is performed using, if necessary, water and additional acidic stream from the scrubbers. The filtrate (F) returns to the waste water treatment, because some colloids are redissolved. so in this process eventually all the toxics metals escape in a stabilized form in the stabilized residues (R) with very limited bio-availability.
Of course the relative amount of water to solids, of acidic liquors to solids, and the feed rate of all the reagents depend very much on the incinerator operating conditions and on the nature of the waste being incinerated. This is optimization and is beyond the scope of this paper.

Results

The washing process above described has been tested at the laboratory level, and in a full scale plant.

Some results have already been disclosed in a former paper delivered at the IT3 2004 conference in Phoenix.in which a similar process, that does not re-integrate the waste water treatment sludge with the fly ash, was presented.

Ash forced washing without sludge integration

The main results, obtained in a full scale plant are given hereunder. The relevant test here is the Swiss leaching test, that involves forced leaching with a CO_2 saturated solution. The Figure 4 shows, in terms of performances, the results when compared to the allowable limit.

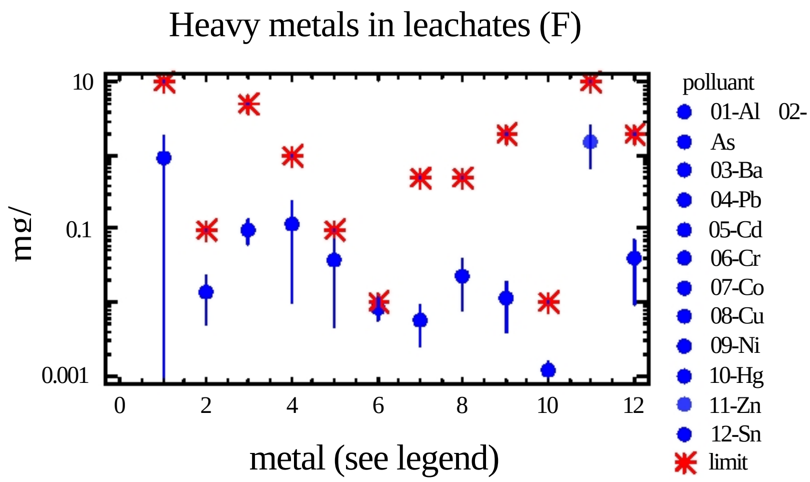

Figure 4

The ecotoxicity tests were also conducted, and the results are given in Table 1.

Table 1

		Raw ash		*Treated ash*		*MEDD 2000*
						limit
Daphnia	CE 50-24h	32.4	OK	89	OK	
	CE 50-48h	21.8	OK	47.6	OK	10
MICROTOX	CE-50-35'	>100	OK	Non toxic	OK	10
Ceriodaphnia	CE20-7d	0.19	**TOXIC**	8.8	OK	1
Algae	CE20-72h	3.7	OK	29	OK	1
Lettuce	CE 50-7d	0.93	OK	Not toxic	OK	
	CE 50-14d	0.95	**TOXIC**	>100	OK	10
Worms	CE50-14d	5.5	**TOXIC**	68.9	OK	

As it can be seen, both the leaching characteristics and the behaviour versus the H14 ecotoxicity test of the treated ash were already good, whereas untreated fly ash failed on both leaching and ecotoxicity tests. It was decided to extend the process

Behavior of the blend fly-ash waste water treatment sludges

The process described previously has been tested at a full size waste to energy plant, and is still in operation. After the necessary tunings had been performed, three kinds of tests were made: Leaching tests, percolation tests, and the ecotoxicity tests. The results can be summarized in the Figure 5 (leaching),

Table 2

Element	leaching limit mg/kg dry	average lixiviation mg/kg dry	min	max	percolation limit mg/l	average c0 conc. mg/l	min	max
		<----- leaching ---->				*<----- percolation ---->*		
Sb	0.7	0.083	0.039	0.140	0.15	0.0013	0.0010	0.0015
As	2 0.166	0.020	0.700	0.3	0.0050	0.0050	0.0050**Ba**	100
	20 0.0883	0.0770	0.1000**Cd**		1 0.0065		0.002	0 .0 2
	0.3	0.0001	0.0001	0.0001				
Cr	10	3.75	0.1210.55		2.5 1.70	1.50	2.00**Cu**	50 0.26
8	0.110.909		30 0.0050		0.0050	0.0050**Hg**	0.2	0.0111
	0.00060.0392		0.03		0.0000	0.0000	0.0000**Ni**	100 0.03
1	0.0010.123		30.005		0.005	0.005		
Mo	10	0.05	0.00	0.11	3.5	0.38	0.18	0.66
Pb	10	0.043	0.0040.102		3 0.065		0.010	0.150
Se	50.018	0.0030.042			0.2	0.051	0.013	0.120
Zn	50	0.24	0.03	1.19	15	0.05	0.02	0.10
Cl-	15000	7753	3480	14196	8500	623	330	940
SO_4--	20000	13489	7644	17667	7000	1433	1400	1500
F	150				40	4.1	0.5	11.0
COD	800				250	1.17	1.00	1.30
pH		11.2	10.7	10.9		9.1	8.1	10.3
conductivity						4433	3000	5600

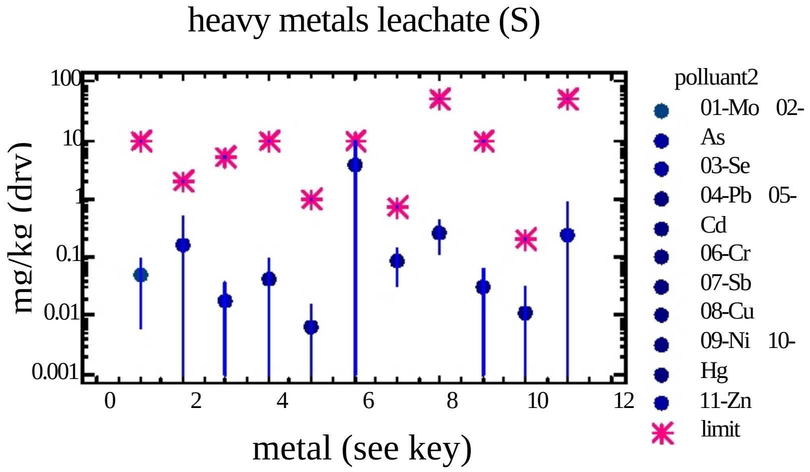

Figure 5: (leaching)

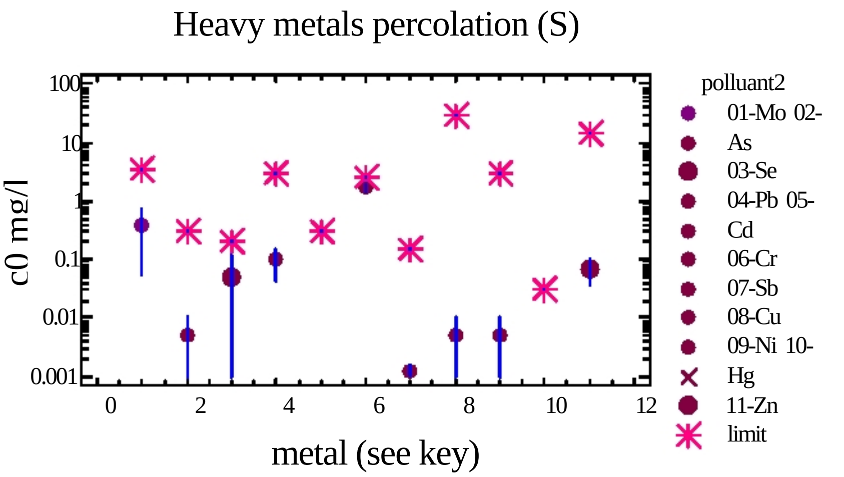

Figure 6 (percolation) ; both Cd and Hg are below 0.001 mg/l.

Table 3 (ecotoxicy)

descriptor					
acute toxicity	Microtox	luminescence	CE 50 5'	non toxic@80%	non toxic@80%
of the leachates		inhibition	CE 50 15'	non toxic@80%	non toxic@80%
			CE 50 30'	non toxic@80%	non toxic@80%
	Daphnia	freezing	CE 50i 24h	[53.8-68.0]	[28.0-34.9]
			CE 50i 48h	[20.6-25.5]	[24.0-29.7]
chronic toxicity	Algae	growth	CEr 20 72h	[7.4-9.2]	[15.8-19.9]
of the leachates	Ceriodaphnia	population	CE 20 7days	[2.2-2.8]	[3.1-4.5]
Lettuce	Lettuce	spouting	CE 50 7days	[15.9-40.8]	[31.8- >100]
		growth	CE 50 14days	[32.7-35.6]	[28.8->100]
Worms	worms	death	CE 50 14days	[32.7-35.6]	[38.7-41.9]

The figure 7 compares the toxicity obtained to the 2002 MEDD limits.

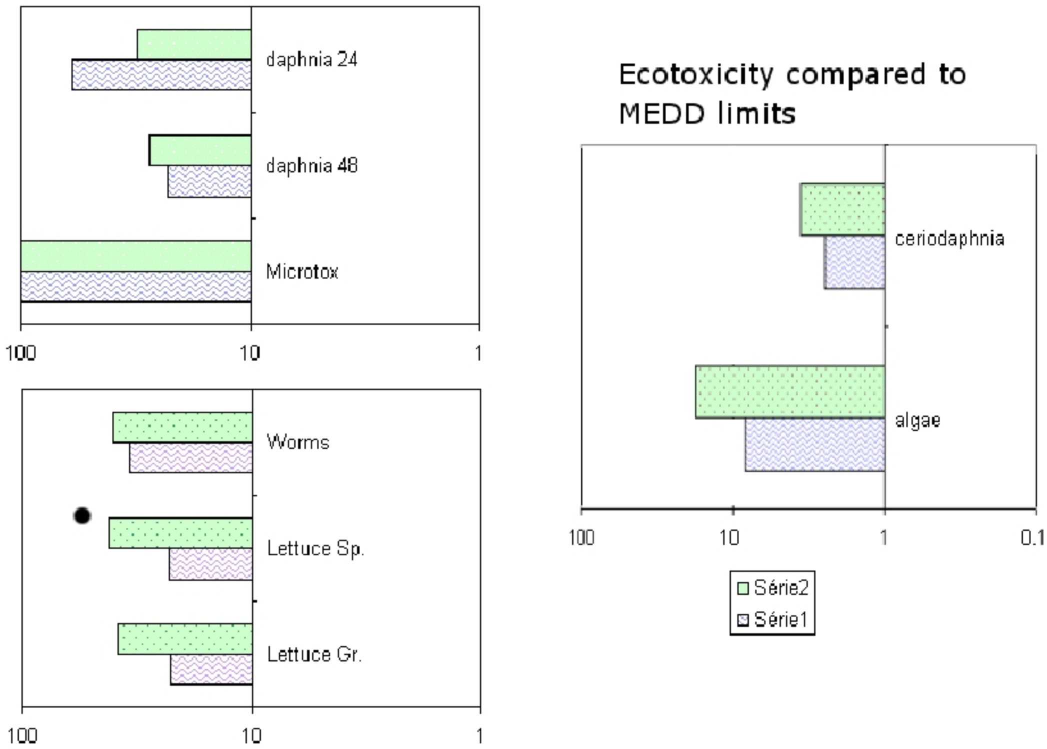

Figure 7

On the left hand side of the vertical bar, the product is considered non toxic, and toxicity increases when moving to the right. The vertical line shows the MEDD limit. It can be seen that again, all the results are well within the specifications, and that, in terms of ecotoxicity the material tested would be not considered as "harmful for the environment"

The final product, as shown on Figure 7 can readily discharged and is easy to handle

Figure 8: final treated residue

CONCLUSION

It is possible to incorporate the sludge from a waste water treatment unit to the fly ashes from a municipal waste incinerator, to submit the resulting blend to a forced leaching that will remove not only the available heavy metals, but that will also stabilize the entire matrix, so that the toxicity to the environment is greatly reduced. After several months of operation on a actual full size plant, it is now demonstrated that the resulting waste stream would not be classified as « harmful for the environment ». This provides an economically attractive solution because only one kind of solids has to be disposed of, and under favorable conditions.

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