DEINKING SLUDGE

Field trial to assess ash leachability and gaseous emissions from boilers firing deinking residue

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ABSTRACT

A field trial was performed to examine the chemistry and leachability of ash and gaseous emissions from boilers burning deinking residue together with natural gas and bark. The results show that, for the boiler firing deinking residue with natural gas, increasing the combustion temperature by increasing the gas flow rate had little effect on NO_x emissions and ash chemistry. Fly ash consisted of mostly calcined clay, CaO and TiO_2. Bottom ash was similar but had higher SiO_2, Fe_2O_3, Na_2O, K_2O, and PbO contents than fly ash. Pb likely originated from clay used as a coating material. Hg was enriched in fly ash and particulates, but its concentration was too small to be of concern. The leachability of both bottom ash and fly ash was low, particularly for boilers that burn deinking residue with bark due to the high CaO content.

Application:

Disposal of ash from boilers burning deinking residue with natural gas, or particularly with bark, should not be a concern because of the low heavy-metal content and the low leachability of the ash.

THE DEINKING PLANT AT Avenor Inc. in Thunder Bay produces about 40 tons/day of deinking residue (sludge) on a dry basis. The residue, as produced, consists of ink components, fillers, degraded fiber, and 45–55 wt.% water. It is burned together with bark in an ABB-CE power boiler fitted with a dump grate (No. 3 boiler) and occasionally in an ABB-CE power boiler originally designed to fire pulverized coal but now modified to fire natural gas (No. 4 boiler). The resulting ashes from these two boilers are mixed and disposed of in the company landfill site and/or are applied as a liming agent on the local agriculture land.

A research project was initiated at the mill in 1992 to evaluate the chemistry and leachability of ash and gaseous emissions from boilers burning deinking residue. It involved (a) laboratory studies to examine the chemical and thermal behavior of the deinking residue and its ash, (b) combustibility tests in a pilot-scale fluidized bed facility, and (c) a field trial to examine the effect of boiler firing conditions on gas emissions and ash chemistry and leachability. Results of the characterization work and combustibility tests have been reported[1, 2]. This paper summarizes results of the field trial and discusses problems associated with ash disposal and emissions.

[1]Latva-Somppi, J., Tran, H. N., Barham, D., *et al., Pulp & Paper Can.* 95(10):T381(1994).

[2]Douglas, M. A., Latva-Somppi, J., Razbin, V. V., *et al., Tappi J.* 77(5): 391(1994).

BURNING DEINKING RESIDUE WITH NATURAL GAS

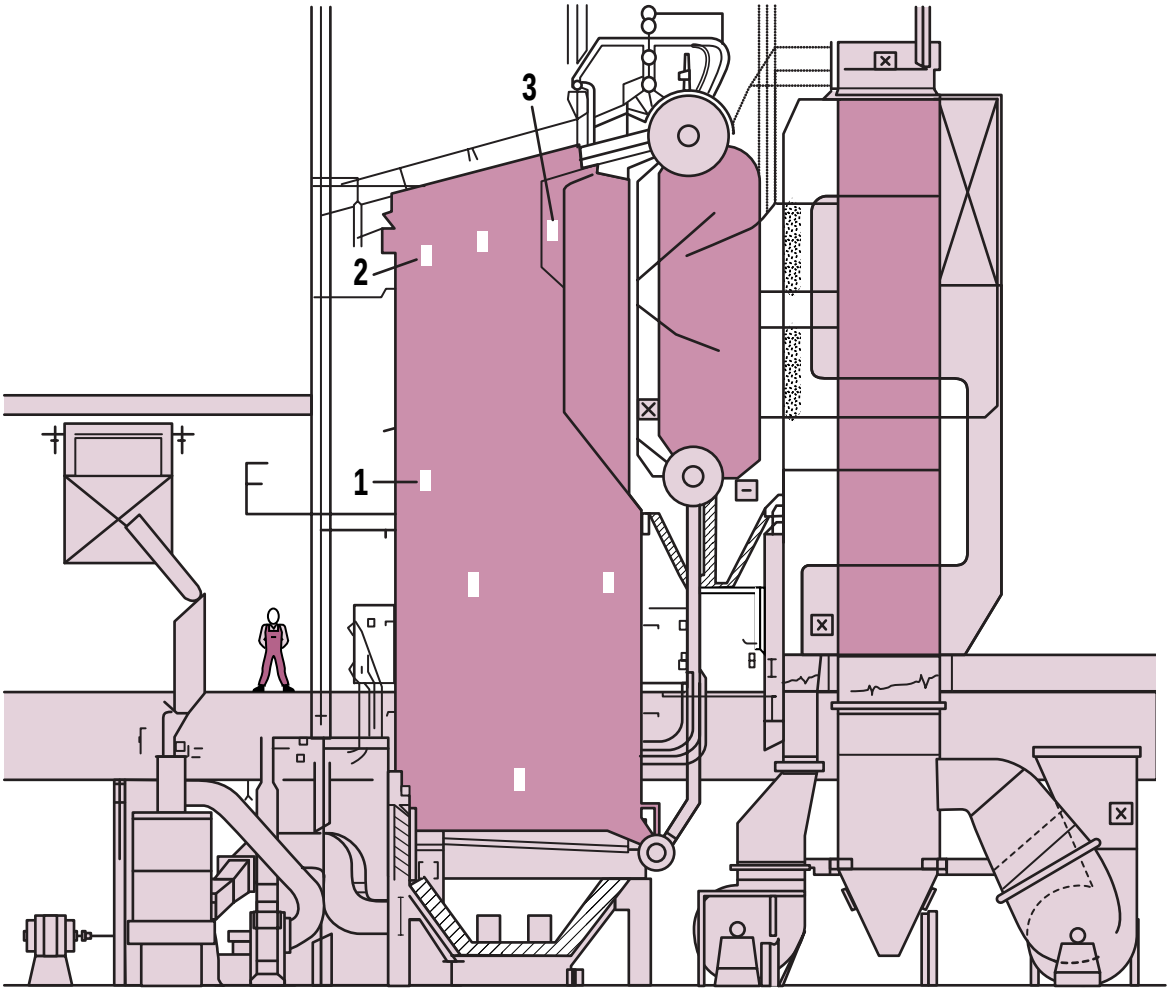
Natural gas is a clean, "ash-free" fuel. From an ash disposal and emissions point of view, burning deinking residue with natural gas can be considered to be similar to burning deinking residue alone. The field trial therefore was conducted mostly in the No. 4 boiler, which burned deinking residue with natural gas.

Figure 1 shows a schematic of the No. 4 boiler, an old coal-fired unit modified for burning natural gas and deinking residue. The residue, at 45–55% dry solids, was transported from the deinking plant by a belt conveyor and deposited onto a reversible belt near the boiler. A wiper assembly on the reversible belt emptied the residue into a chute connected to a vertical pipe. The wiper arm was operated by an air cylinder that could turn the residue flow to the boiler on and off. The vertical pipe allowed the residue to fall by gravity approximately 13.5 m (40 ft) into the inlet of a coal pulverizer transporting the residue through the existing coal pipes toward the tangential windbox located about halfway up the furnace chamber of the boiler.

The air stream that entrained the residue was drawn by the exhauster fan through the tubular air heater and pulverizer. The air was preheated, and the temperature of the air/residue mixture was controlled at about 93°C (200°F). The residue was thus air dried to some degree before being discharged into the boiler slightly above the tangential fireball created by natural gas guns. This method of transporting deinking residue was developed by the mill personnel. While unconventional, it proved to be quite reliable.

Trial procedures

To examine the effect of combustion temperature on ash chemistry and gaseous emissions, during the trial the deinking residue flow rate was fixed at 2400 L/min, while the gas flow rate was varied from 60,000 to 130,000 standard ft^3/h (SCFH) (**Table I,** Tests A, B, C, and D). A "blank" test was also performed to examine the effect of burning natural gas alone at 100,000 SCFH on flue gas temperature and gaseous



I. Schematic of the No. 4 boiler and locations of temperature measurements

Test	Gas flow rate, SCFH	Deinking residue flow rate, L/min
A	60,000	2,400
B	80,000	2,400
C	100,000	2,400
C′	100,000	0
D	130,000	2,400

I. Fuel flow rates during trial in the No. 4 boiler

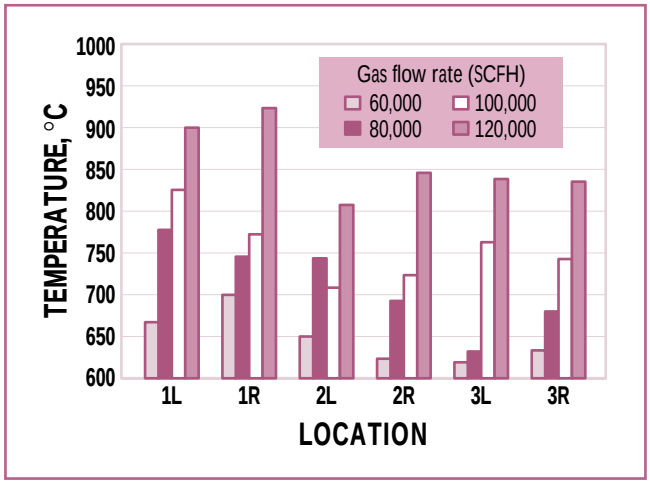
emissions (Test C).

At each fuel flow condition, the boiler was operated for 3–6 hours. During the test, flue gas temperatures and gas emissions were measured, and samples of the bottom ash and fly ash were collected and subjected to chemical analysis and leachability tests. Samples of particulate were also collected at a location near

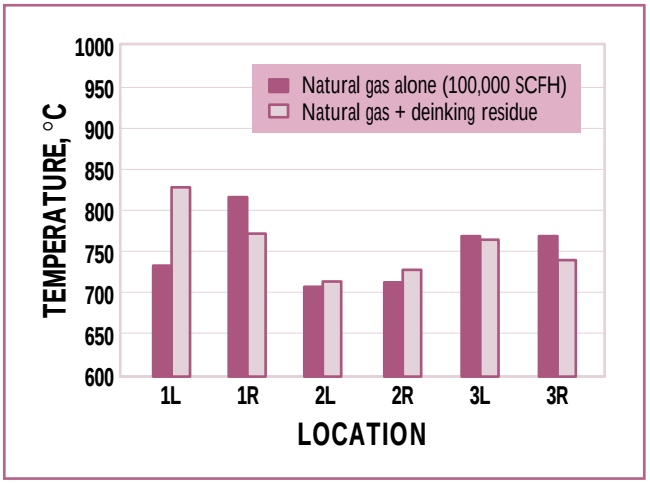
Component	Bottom ash, wt. %	Fly ash, wt.%
SiO_2	49.8	45.0
Al_2O_3	21.0	34.2
CaO	8.5	8.9
MgO	1.7	2.1
TiO_2	3.5	6.0
Na_2O	3.3	0.4
K_2O	0.4	0.2
P_2O_5	0.2	0.2
Fe_2O_3	9.2	0.8
LOI*	1.5	1.2
Total	99.0	99.1

* Loss on ignition

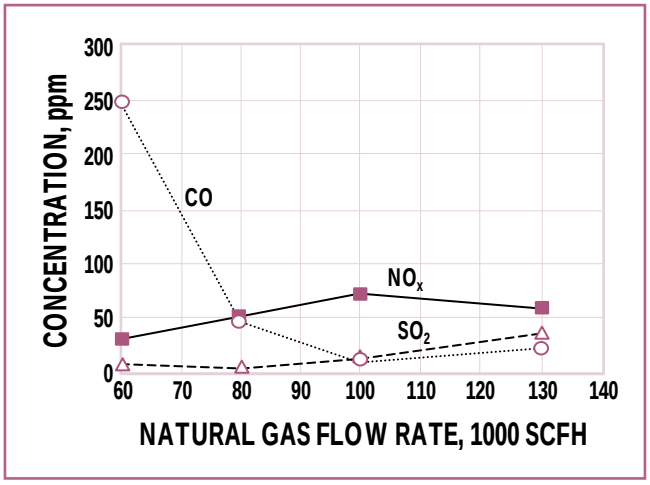
II. Major components of bottom ash and fly ash samples collected from the No. 4 boiler after Tests A, B, C, and D



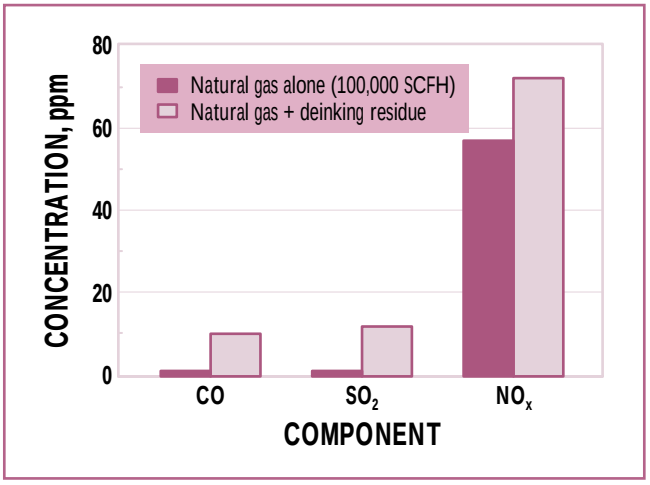
2. Flue gas temperatures at various locations in the No. 4 boilers during tests with different natural gas flow rates



3. Flue gas temperatures at various locations in the No. 4 boilers during tests C and C′



4. CO, NO_x, and SO_x concentrations in the No. 4 boiler flue gas during tests (raw data)



5. CO, NO_x, and SO_x concentrations in the No. 4 boiler flue gas during tests C and C′

the boiler stack during selected tests. Leachability tests were performed according to the Ontario Ministry of Environment (MOE) Procedure—the 1993 Environmental Protection Act Regulation 347. Elements examined included mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As), and other heavy metals.

Flue gas temperatures

The flue gas temperatures were measured at six locations [1L, 2L, 3L (left wall), 1R, 2R, and 3R (right wall)] using a temperature probe. The temperature readings were calibrated against results obtained using a suction pyrometer. **Figure 2** shows corrected temperatures at these locations at various gas flow rates. The flue gas temperature at all locations increased markedly with natural gas flow rate. At location 1L, for instance, the flue gas temperature increased from 665°C (1230°F) to 900°C (1650°F) as the natural gas flow rate was increased from 60,000 to 130,000 SCFH.

Figure 3 shows flue gas temperatures at these locations when the boiler was burning natural gas alone, i.e., no deinking residue, at a flow rate of 100,000 SCFH (Test C′), and flue gas temperatures during the time when the boiler was burning deinking residue together with natural gas at the same flow rate. No significant change in temperature was found.

Gaseous emissions

The flue gas composition was measured at a location after the induced draft fan using a portable gas analyzer. The results for CO, NO_x (NO and NO_2), and SO_2 are shown in **Fig. 4**. The CO concentration in the flue gas decreased markedly from 250 to 50 ppm as the natural gas flow rate was increased from 60,000 to 80,000 SCFH and decreased further to 20–30 ppm during tests at higher natural gas flow rates. From the results, it appears that a natural gas flow rate of at least 80,000 SCFH is required for effectively burning the

Component	Bottom ash, ppm	Fly ash, ppm	Particulate, ppm	Bottom ash leachate, ppm	Fly ash leachate, ppm
Hg	0.002	0.009	0.051	<0.005	<0.005
Pb	147	8	80	<0.02	<0.02
Sc	9	14	6	<0.01[a]	<0.01
V	59	72	45	0.05	0.04
Cr	95	56	50	<0.01	<0.01
Be	2	1	1	<0.01	<0.01
Mn	397	76	43	0.2	0.1
Co	335	315	1	<0.01	<0.01
Ni	99	63	39	0.02	0.02
Cu	627	395	800	0.04	0.02
Zn	361	331	1196	0.4	0.9
As	<3	<3	<3	<0.03	<0.03
Rb	19	10	N/A[b]	N/A	N/A
Sr	159	98	47	0.4	0.3
Y	<10	<10	<10	<0.01	<0.01
Zr	123	124	28	<0.01	<0.01
Nb	32	39	N/A	N/A	N/A
Mo	3	1	4	0.06	0.05
Ag	2	2	1	<0.005	<0.005
Cd	2	<1	1	<0.01	<0.01
Sn	25	12	17	<0.01	<0.01
Sb	<5	<5	<5	<0.05	<0.05
Ba	329	387	220	<0.3	<0.4
La	31	45	22	<0.01	<0.01
Ta	5	3	2	<0.02	<0.02
W	315	96	8	<0.1	<0.1
Bi	<3	<3	<3	<0.03	<0.03

[a] <0.01: below detection limit of 0.01 ppm
[b] N/A: not available

III. Minor components of bottom ash, fly ash, particulate, and their leachates from the No. 4 boiler after Tests A, B, C, and D

deinking residue (2400 L/min) in the No. 4 boiler.

The NO_x and SO_2 concentrations were low. They increased only slightly with an increase in the natural gas flow rate. During the test at 130,000 SCFH natural gas flow rate, the NO_x concentration remained low at 60 ppm, despite the high flue gas temperature recorded during this test. This temperature independence of NO_x emissions suggest that NO_x in this case was formed from fuel nitrogen and was not thermal NO_x.

Figure 5 shows concentrations of CO, NO_x, and SO_x in the flue gas during tests when the boiler was burning natural gas at a flow rate of 100,000 SCFH, with and without deinking residue (Tests C and C´). The concentrations of these gases were clearly higher when the deinking residue was burned.

Ash composition and leachability

Chemical analysis was performed on all bottom ash and fly ash samples. For particulate samples, only minor components were analyzed due to the small quantity of the samples collected during the trial. The results showed no significant change in ash and particulate compositions with natural gas flow rate (or combustion gas temperature).

Table II summarizes the averaged values, expressed as oxides, of major components (>0.1 wt.%) of the bottom ash and fly ash samples collected from all tests. The fly ash consisted of mostly SiO_2, Al_2O_3, CaO, and TiO_2 and small amounts of MgO, Na_2O, K_2O, P_2O_5 and Fe_2O_3. Note that the SiO_2/Al_2O_3 molar ratio of the fly ash was 2.2, close to that of calcined clay ($Al_2O_3 \cdot 2SiO_2$). This implies that these oxides were derived from clay used as a coating material. CaO, MgO, and TiO_2 were respectively derived from $CaCO_3$, talc, and titanium dioxide used as coating/ whitening materials. The bottom ash was similar but had a higher SiO_2/Al_2O_3 molar ratio (4.0) and a significantly higher Fe_2O_3 content (9.2 wt.%) than fly ash. This was probably due to the fact that the furnace bottom tends to collect large and heavy materials included in the deinking residue, such as sand particles (SiO_2), staples, and scrap metal.

Table III shows the averaged concentrations of minor components of the bottom ash, fly ash, and their leachate. Of these components, Hg, Pb, As, and Cd were of particular

Component	Clay 1, ppm	Clay 2, ppm	Clay 3, ppm
Hg	0.4	<0.2	0.08
Pb	15	105	0.17
Cr	83	83	120
Mn	2	5	N/A
Co	1	9	N/A
Ni	13	105	16
Cu	7	21	13
Zn	8	62	26
As	1	2	0.7
Sr	83	165	N/A
Ag	1	N/A	N/A
Cd	<0.1	0.2	0.02
Sn	5	39	210
Sb	<0.1	0	N/A
Ba	37	1344	N/A
Bi	<0.1	<0.1	N/A

IV. Minor components of clays

Component	BARKING/DEINKING RESIDUE FLOW RATIO 1:1 (Test E)	2:1 (Test F)
SiO_2	36.2	33.4
Al_2O_3	10.3	9.2
CaO	32.9	34.7
MgO	4.2	4.4
TiO_2	0.9	0.8
Na_2O	1.2	1.0
K_2O	2.4	2.6
P_2O_5	1.5	1.6
Fe_2O_3	5.8	5.9
LOI	3.3	3.9
Total	98.7	97.4

V. Major components of the No. 3 boiler bottom ash. Results in wt.%

interest due to their potential environmental impact. These elements were present in low concentrations in both bottom ash and fly ash, and were below their respective detection limits in the ash leachate. Note from Tables II and III that the bottom ash contained more Pb, Na, and K than fly ash, due presumably to the lower temperature at the furnace bottom. The bottom ash contained less Hg than fly ash and particulate (Table III), due probably to the high volatility of Hg. Although Hg was enriched in particulate, the concentration was too small (51 ppb) to be of concern.

Since clay is the major component of the ash, its composition should have an effect on the ash composition. **Table IV** shows minor components of three different clays used as paper fillers. Note that the Pb content varies widely. Clays 1 and 2, respectively, contained 15 ppm and 105 ppm of Pb, whereas Clay 3 contained only 0.2 ppm. The relatively high Pb content in the ash found in this study was probably a result of clay inclusion in the ash. Pb and other heavy metals, however, are likely in the form of oxides that are bound within the clay structure and are thus unleachable. They should not be a concern from an ash disposal point of view.

BURNING DEINKING RESIDUE WITH BARK

For comparison purposes, two tests were also performed to examine the chemistry and leachability of ash from the No. 3 boiler, which burned deinking residue with bark. The boiler is stoker fed and has a dump grate at the furnace bottom. It was normally operated at a deinking residue/bark ratio of 1:3. During the trial, the amount of deinking residue was increased by increasing the deinking residue/bark ratio to 1:2 (Test E) and then 1:1 (Test F) so that the maximum effect of the residue on ash properties could be examined. Natural gas was also burned at a flow rate of 5000 SCFH during the tests to ensure proper combustion.

Table V shows the major components of bottom ash samples collected from the No. 3 boiler during Test E and Test F. Compared to the bottom ash from the No. 4 boiler, the bottom ash from the No. 3 boiler had higher CaO and K_2O contents due to the high concentrations of these materials in the bark. **Table VI** shows the minor components of the bottom ash samples and leachates. Similar to the results obtained for No. 4 boiler, Hg, Pb, As, and Cd concentrations were very low in the ash and were all below their respective detection limits in leachate.

The solubility of heavy metals in water generally decreases as the pH of the solution increases. The ash leachability thus is expected to be lower for boilers burning deinking residue with bark due to the higher alkalis content of the ash.

CONCLUSIONS

A field trial was performed at Avenor Inc. to assess potential problems associated with ash disposal and emissions from boilers burning deinking residue with natural gas and bark. The results show that:

- Increasing natural gas flow rates resulted in no increase in NO_x emissions and no appreciable change in ash composition with natural gas flow rate.
- Bottom ash has a composition similar to fly ash but contains more SiO_2 (from sand) and Fe_2O_3 (from scrap metal) than fly ash. Bottom ash also contains more Pb, Na, and K than fly ash, presumably due to the lower temperature at the boiler bottom.
- Pb likely originated from clay used as a coating material. It is bound in the clay structure and is

Component	Test E Ash, ppm	Test F Ash, ppm	Test E Leachate, ppm	Test F Leachate, ppm
Hg	<0.005	<0.005	<0.005	<0.005
Pb	<2	<2	<0.02	<0.02
Sc	9	9	<0.01[a]	<0.01
V	74	71	0.05	0.04
Cr	81	55	<0.01	<0.01
Be	1	1	<0.01	<0.01
Mn	6570	6170	0.05	<0.01
Co	171	780	<0.01	<0.01
Ni	43	42	<0.01	<0.01
Cu	92	93	<0.01	<0.01
Zn	361	331	0.4	0.9
As	<3	<3	<0.03	<0.03
Rb	37	40	N/A[b]	N/A
Sr	795	713	4.8	5.3
Y	730	629	<0.01	<0.01
Zr	7	7	<0.01	<0.01
Nb	13	11	N/A	N/A
Mo	4	1	<0.01	<0.01
Ag	2	2	<0.005	<0.005
Cd	2	<1	<0.01	<0.01
Sn	<10	<10	<0.1	<0.1
Sb	<5	<5	<0.05	<0.05
Ba	3,140	2,980	12	13
La	15	17	<0.01	<0.01
Ta	4	2	<0.02	<0.02
W	1,010	2,860	<0.1	<0.1
Bi	<3	<3	<0.03	<0.03

[a] < 0.01: below the detection limit of 0.01 ppm
[b] N/A: not available

VI. Minor components in the No. 3 boiler bottom ash and leachate

KEYWORDS
Ash, bark, boilers, chemical composition, chemical elements, combustion, deinking, emission, gas, heating equipment, leaching, metals, natural gas, plant tissues, residues, separation, sludge, solid wastes.

unleachable. Hg was enriched in fly ash and particulate, but the amount was too small to be of concern.

- The bottom ash from the No. 3 boiler firing deinking residue with bark had higher CaO and K_2O contents than that from the No. 4 boiler firing deinking residue with natural gas. Hg, Pb, As, and Cd concentrations were very low in the bottom ash and were all below their respective detection limits in the leachate.
- From an ash leachability point of view, disposal of ash from boilers burning deinking residue with natural gas or bark should not be a concern. **TJ**

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