

TREATMENT OF RESIDUES FROM AIR POLLUTION CONTROL SYSTEMS

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ABSTRACT

The residues from air pollution control systems on waste incinerators are typically deemed to be a hazardous material due to the potential for leaching of trace metals and salts. As a result, in many countries these residues require special handling, treatment and/or disposal. An innovative technology has been developed to recover useful by-products from these residues and render the remaining residue non-hazardous, thereby eliminating the long-term environmental liability associated with disposing of these materials.

The primary by-products of the patent pending APEX Treatment System include, a non-hazardous calcium enriched solid suitable for construction applications, a highly concentrated lead residue suitable for recycling to smelters and a commercial grade calcium chloride solution. This paper focuses on the results from a large-scale demonstration project.

INTRODUCTION

Background

The incineration of municipal solid waste (MSW) typically results in a 90% reduction in volume, and a 60 to 75% reduction in weight of the material (IAWG, 1997). The practice also results in the formation of hydrogen chloride (HCl) and sulphur dioxide (SO₂) in the flue gas stream. During the late 1970's and early 1980's, concern over the emissions of these acid gases and other by-products of MSW combustion resulted in the development of more efficient incinerator operating conditions and improved air pollution control technologies. In turn, this enhanced ability to minimise emissions has resulted in the capture of greater volumes. In most countries around the world, APC residues are classified as a hazardous waste because of the high potential of the residue to leach readily soluble salts and potentially soluble trace metals. Moreover, these residues also contain trace levels of polychlorinated dibenzo-p-dioxins (PCDD), dibenzo-furans (PCDF), and polyaromatic hydrocarbons (PAHs) which may be of regulatory concern in some jurisdictions. These

of hazardous residues in modern air pollution control (APC) systems. Approximately 70% to 95% of the total ash generated from an incinerator is bottom ash, whereas the remaining 5% to 30% is fly ash residue captured in APC systems.

To comply with new stringent air emission regulations, modern APC systems are designed to cool and chemically condition the flue gases (Environment Canada, 1986). Cooling is facilitated by a humidifying spray of water to reduce temperatures to 160°C - 170°C. This cooling operation promotes condensation of vapour phase contaminants and promotes subsequent chemical reactions. Chemical conditioning of the flue gases is generally facilitated by the injection of powdered hydrated lime, or some other form of caustic solution, into the flue gas stream to act as an acid gas sorbent and provide reactive surfaces for condensation of volatile compounds.

There are two predominant types of APC systems: i) wet scrubbers and ii) dry or semi-dry lime injection. In dry/semi-dry lime injection APC systems, the calcium hydroxide (Ca(OH)₂) reacts with the acid gases to form significant concentrations of calcium chloride (CaCl₂) and calcium sulphate (CaSO₄) that comprise the bulk of the APC residue waste stream. The resulting CaCl₂ and excess lime present in the APC residues are quickly solubilised upon contact with water. Furthermore, since the stoichiometric ratio of lime addition is greater than 1, the APC residues are highly alkaline and the potential to solubilise amphoteric metal compounds (such as some Pb compounds) is greatly increased. Consequently, leachates from these residues may contain high concentrations of salts and trace metals, such as Al, Cr, Pb and Zn.

characteristics quite often necessitate that APC residues be disposed as a hazardous waste at considerable cost to municipalities and their contracted agents. It is often argued that landfill solid waste diversion and energy recovery benefits derived from EFW incineration facilities are adversely affected by the requirement to dispose of a hazardous residue that may have long-term negative environmental implications. As a consequence

of these concerns, disposal of APC residues is one of the major issues limiting the acceptance of new municipal energy-from-waste incinerator facilities.

APEX Treatment System

Currently, there are several generic types of ash treatment processes, such as additive-based technologies (solidification/stabilisation), and thermal-based processes. However, acceptance of these technologies has been limited by potential long-term environmental implications and costs. To address the need for cost effective and environmentally sound APC residue treatment, the APEX Treatment System (patent pending) was developed. The APEX technology is based on controlled washing, dewatering and rinsing operations that remove highly soluble amphoteric metals and salts from APC residues. The remaining dewatered residue generated from this treatment process meets the criteria for a non-hazardous material (e.g., Ontario Regulation 347, the Canadian Transportation of Dangerous Goods Leaching Procedure, the US Toxicity Characteristic Leaching Procedure and the Japanese Leach Test).

The treated filter cake can be rendered suitable as an amendment for aggregate feedstock for use in concrete/asphalt manufacturing and in certain ceramics

- Constructing a mobile APEX Treatment System demonstration facility capable of handling 1 dry-tonne of
- Operate, monitor and modify the operating parameters to attain the best operating conditions for the efficient recovery of
- Undertake a product sampling and testing program to accurately characterise by-product composition profiles over an extended period
- Identify, assess, and forecast the potential ongoing maintenance requirements for a full-
- Gather and assess demonstration-scale treatment system operating data over an extended period to develop a full-scale engineering design specifications and automated process control algorithms for standard operating procedures.

The demonstration trailer was set up at a full-scale EFW facility consisting of three parallel two-stage modular combustion units. The air pollution control system is a lime-based "dry" system, consisting of humidifying water-spray and dry powdered lime injection in conditioning towers, followed by fabric-filter dust collectors.

APC Residue Sample Collection

APC residue was collected for treatment from storage bunkers underneath the fabric filter units prior to each day's test runs. An industrial vacuum system was used to draw the residues from the bunker into four 200 L

applications. The trace metals solubilised during the washing stage are then precipitated and separated from the rest of the filtrate. The metal precipitate, primarily lead salts, may be utilised as a feedstock product by lead smelting operations. The post-precipitate filtrate can be further processed to generate a concentrated calcium chloride (CaCl_2) solution that is commonly used for road construction, dust control, de-icing or as an anti-foaming agent in the pulp and paper industry.

Objectives

A large-scale demonstration project was undertaken to evaluate the technical and economic viability of the APEX Treatment System. The broad objectives included gathering sufficient representative large-scale operating data to facilitate detailed engineering design and costing for full-scale APEX Treatment Systems. Testing was also required to demonstrate and optimise the capability of the APEX technology to produce non-hazardous or recyclable by-products that meet regulatory and commercial quality specifications under representative operating rates.

The specific objectives of the demonstration project included:

APC residue over an 8 hour operating period.

recyclable products from APC residue;

and under different incinerator operating conditions;

scale APEX Treatment System;

barrels for transport to the trailer as required. The selection of the incinerator line (A, B or C) was dependent on the amount of APC residue present in the storage bunker, the on-line availability of the particular incinerator unit and ready accessibility to the bunkers. Samples from each of the three incinerator lines were collected over the duration during the demonstration program to generate a cross-section of data on the APC residue quality.

METHODOLOGY

Field Demonstration of System

The field demonstration trials were conducted over an extended operating period between August and December 1998. Prior to operating at continuous full operating rates, preliminary tests were performed to set the benchmark for optimal operating conditions for each of the three key processing stages of the APEX

Treatment System. Once confirmed, 37 full test runs were conducted using the same operational control parameters. The demonstration was carried out under Ontario Ministry of the Environment Certificate of Approval No. 620208.

Sampling of By-products

All by-products generated from the demonstration unit were sampled during each day of demonstration-scale processing.

Filter-cake

After washing, rinsing and air blowing for each test run, the filter-cake was sampled by retrieving full depth cross-sections of each filter cake from random areas of the filter plate chambers. Sufficient material was collected from each filter-plate cake to generate at least 7.5 kg of composite sample per test run. These samples were placed into separately labelled 4- quart plastic bags for storage and transport to the laboratory. 1.5 cm diameter core samples were extracted from the samples at random using a stainless steel sampling tube to obtain sufficient samples for testing using the Regulation 347 Leach Procedure (Government of Ontario, 1995).

Metal Precipitate

All of the metal precipitate generated during the demonstration trials was collected and archived for laboratory testing. Typically, several test runs were conducted prior to recovering the precipitate from the filter press. Samples required for chemical composition were obtained from the archived composites via randomly sampled 1.5 cm diameter cores.

Post Metal Precipitation Filtrate

Filtrate from the metal precipitation process was directed to a large tank for storage. Composite samples of several test runs were allowed to collect prior to being slowly discharged through a cartridge and activated carbon filter to the sanitary sewer, as per the Certificate of Approval. Four 200 L barrels of composite filtrate (post polishing filters) were collected and archived for further testing.

Chemical Composition

Metal Cations Testing

Samples of the untreated APC residue, treated filter cake, and subsequent process solid and liquid streams were analysed for the following metal cations:

aluminum, arsenic, barium, boron, cadmium, calcium, chromium, copper, lead, mercury, potassium, selenium, sodium, and zinc.

The solid samples were digested using aqua regia/hydrofluoric acid and hydrogen peroxide prior to analyses for most trace metals. The digested solid

samples and the leachates were analysed using inductively coupled plasma spectroscopy, direct coupled plasma spectroscopy, flame atomic absorption (AA) or flame AA with graphite furnace. Analyses of As and Se were performed using hydride generation. These methods are described in the Wastewater Technology Centre's Manual for Laboratory Analytical Methods (WTC, 1993).

Physical Tests

Moisture Content

The moisture contents of the untreated APC residue and treated filter cake were determined by weight loss of a sample at 60°C for 24 hours as required by Regulation 347 to account for moisture in the filter cake.

Total Dissolved Solids

The Total Dissolved Solids (TDS) of the filtrate from the wash/rinse process were determined by pre-filtering the samples through a 0.45µm filter prior to adding a known volume of liquid sample to a pre-weighed container. The sample was then evaporated to dryness and the container is cooled and re-weighed. The difference in weight of the container before and after the sample is evaporated represents the Total Dissolved Solids content of the sample.

Ontario Regulation 347 Leach Procedure

The Ontario Reg 347 Leach Procedure (Government of Ontario, 1995) is used by the Ontario Ministry of the Environment to classify materials as a hazardous, registered or un-registered waste. The test involves slowly mixing a 50 g sample of material in a minimum of 800 mL of distilled water at a pH of 5.0 or less, for 24 hours. The maximum amount of acid addition allowed to achieve pH 5.0 ± 0.2 is 2.0 milliequivalents of acetic acid per gram of waste (200 mL of 0.5 N acetic acid). The test was conducted on the raw APC residue and treated filter-cake, all of which required no special sample preparation. In all cases, the entire 2.0 milliequivalents of acid were added to the mixture after the first hour. The samples were filtered through 0.45 micron filters, prior to preserving the leachates to a pH of 2.0 using concentrated nitric acid.

Statistical Analysis

In general, the data generated from the demonstration project was analysed using standard statistical techniques including (mean, standard deviation, median, variance, and 95 % confidence intervals).

The different statistical parameters used here include:

Mean - the arithmetic mean is the sum of all data points within a specified set, divided by the number of data

points or counts within the set. The mean is typically used when data sets are considered normally distributed.

Median - the 50th percentile, or the mid-data point within a sorted data set. This measure is often used if data sets are not normally distributed.

Mode - The value in a data set that appears more frequently than any other value. The mode emphasizes data concentration and is best used to describe large data sets.

Standard Deviation - the square root of the variance of the data set. The standard deviation determines how much individual values in a data set differ from the mean of the data set. It is typically used to verify the reliability of the mean, i.e., the lower the standard deviation in comparison to the mean, the more appropriate the use of the mean is to depict the data set.

Variance - the variance of the data set (excluding "Nil" values) using the n method (biased).

Skewness - Characterises the degree of asymmetry or "shape" of a distribution around its mean. A "0" result indicates that the distribution is symmetrical about the mean.

Inter-quartile Range- the 25th to 75th percentiles. These values are often used to indicate differences between data sets, i.e., if the inter-quartile ranges overlap significantly, then the data sets can be considered similar.

Confidence Interval - indicates that the population mean will be within an interval (\pm) around that mean for the given distribution with a specific degree of confidence and determines the margins of error.

RESULTS

APC Residue

The APC residue was sub-sampled and subjected to different tests to provide a baseline set of data for comparison purposes.

Solubility

Test data from the benchmark trials indicate that approximately 25 - 38% of the raw APC residue was solubilised during the washing and rinsing process. Consequently, 62 - 75% of the residue remained as a calcium enriched filter cake. The range of dissolution during the demonstration trials was approximately 30 -

33% of the weight of the raw APC residue. This was relatively consistent over the course of the demonstration program..

Density

The uncompacted bulk density of the raw APC residue was 0.3 g/cm³ (dry weight basis), whereas the density of the treated residue was 1.36 g/cm³ (at approximately 40% moisture content).

Ontario Regulation 347 Leach Procedure

Samples of the raw APC residues were subjected to the Ontario Regulation 347 Leach Procedure to provide a benchmark for comparison against treated APC residue. The summary of the test results on elements of concern are provided in Table 1.

The results indicate that the concentrations of the elements Cd, Hg, As, Se, B, Ba and Cr in leachates from both the raw and treated residues are well under the regulatory limits. It should be noted that the endpoint pH of the leachates was typically >12.3 for tests on both raw and treated residue, thereby eliminating pH as a confounding factor affecting the results of the test.

Pb concentrations in the leachates from the raw residue samples indicate that the raw residue would be defined as a "leachate toxic" waste, requiring disposal as a hazardous waste. Conversely, the residues samples from the APEX treated filter cakes generate leachates which are typically below the limit as a "leachate toxic" waste (i.e., < 5.0 mg/L of Pb). The standard deviation of the Pb concentrations (1.77 mg/L) was less than the mean (2.07 mg/L) and about the same as the median value (1.73 mg/L). The data set was slightly skewed, which is consistent with the data illustrated in Figure 3. Figure 1 presents the distribution of Regulation 347 results counts based on 0.5 mg/L concentration intervals. The data clearly indicates that data is not normally distributed, with the overwhelming majority (86%) of the samples tested were less than 3.0 mg/L of Pb. Of that percentage, 21 samples were measured at less than 1.0 mg/L of Pb, and 44 samples were measured at less than 2.0 mg/L of Pb.

The data set was sufficiently large to generate a mode value, hence, the mode could be used to describe the data population (1.05 mg/L). The 95% confidence level indicates a potential 40% margin of error, however, this would be expected given the broad range of data values. The interquartile range was defined by 0.988 - 2.51 ppm of Pb.

Table 1. Statistical Summary of Regulation 347 Leach Procedure Results on Raw and Treated APC Residues (mg/L)

Analysis	End pH	Pb	Cd	Hg	As	Se	Ba	Cr
Raw Residue								
Mean	12.35	52	0.0011	0.0066	0.001	0.0165	0.799	0.023
Median	12.33	58	0.0014	0.0020	0.001	0.0147	0.919	0.024
Std. Dev.	0.05	16.82	0.0024	0.011	0.0006	0.011	0.399	0.0145
Variance	0.0025	283	0.0001	0.0001	0.00001	0.00011	0.159	0.0002
Skewness	0.163	-0.46	1.78	1.72	0.41	0.68	-0.85	0.1
Minimum	12.3	26.3	BD	BD	BD	BD	BD	BD
Maximum	12.4	74.7	0.0063	0.032	0.00178	0.033	1.19	0.044
Count	10	12	10	10	10	10	10	10
Cnf. Level (95%)	0.031	9.51	0.0014	0.006	0.00033	0.0059	0.226	0.0082
Treated Residue								
Mean	12.36	2.07	0.0032	0.003	0.0012	0.094	0.262	0.052
Median	12.40	1.73	0.0015	0.0023	0.001	0.014	0.26	0.051
Mode	12.40	1.05	0.0015	0.0012	0.00072	0.00945	0.224	0.035
Std. Dev.	0.20	1.77	0.0057	0.0023	0.0007	0.0059	0.0485	0.019
Variance	0.038	3.12	3×10^{-5}	5×10^{-6}	5×10^{-7}	0.00004	0.0024	0.0003
Skewness	-3.10	1.14	5.08	1.74	4.67	-0.04	1.60	0.25
Minimum	11.40	0.032	0.0012	0.0009	1×10^{-5}	0.0007	0.184	0.0167
Maximum	12.54	7.19	0.039	0.010	0.006	0.026	0.469	0.10
Count	72	72	72	72	72	72	72	72
Cnf. Level (95%)	0.045	0.41	0.0013	0.0005	0.0002	0.0014	0.011	0.0043
Reg. Limits								
Leachate Toxic		> 5.0	>0.5	>0.1	>5.0	>1.0	>100	>5.0

BD = below detection

Figure 2 depicts the concentration of Pb in the Regulation 347 Leach Procedure versus the test runs. It should be noted that 6 of the 8 samples which generated leachates with Pb concentrations marginally higher than 5.0 mg/L came from test runs (21 - 23) conducted on ash from Incinerator Line A which had been shut down for repair 2 days prior to the sampling (reason for the shut down was unknown). Despite the fact that these data points appear as a comparatively discrete set of data within the overall data population, the difference could not be attributed to the operation of the APEX Treatment System, since no significant operational changes were made during those test runs. It is difficult to attribute variations in incinerator operating control parameters, such as lime addition rates, temperature variations in the fabric filter unit and previous incinerator upsets, as this type of data was not available.

Irrespective of the selected indicator (mean, median, mode, interquartile, etc.), the overall results indicate that data population is well below the regulatory limit of 5.0 mg/L of soluble Pb.

Metal Precipitation

As mentioned previously, during the APC residue washing/de-watering process, approximately 30-33% of the APC residue is solubilised. The filtrate from the filter cake contains mostly chlorides (calcium, sodium, potassium), carbonates, and sub-percent levels of soluble hazardous metals (such as Cr, Al, Zn and Pb). Since

these elements are undesirable contaminants in the final CaCl_2 by-product or any wastewater discharge stream, it is necessary to remove the metals from the liquid phase.

The APEX Treatment System makes use of a proprietary method to efficiently remove trace metals from the brine filtrate. The process yields a yellow precipitate which is then removed from the process stream using a filter press. All of the precipitate generated during the demonstration program was collected for analysis. Composite samples from the different runs were submitted for elemental composition. The results are given in Table 2.

The results indicate that the metal precipitation process is quite effective at generating a consistent quality of lead-based precipitate. The concentration of Pb in the precipitate was about 65% by weight for most of the test runs. The precipitate also contained about 4% zinc, about 0.3% copper and about 0.26% Cr. Trace amounts of Cd, Hg and As were also measured in the precipitate.

Table 2. Summary of Chemical Composition of Composite Metal Precipitate Samples (mg/kg)

Run	Pb	Cd	Cr	Ni	Zn	B	Cu	Al	Hg	As	Se
Comp 1-6	641000	20.7	1720	354	56200	23.2	2600				
Comp 5-6	687000	7.36	6050	1370	35700	78.9	3740	1400	82.7	7.19	0.567
Run 7	647000	7.1	2210	417	35000	30.4	4540				
Comp 8-10	581000										
Comp 15-17	631000	6.47	531	77.8	42100	21.5	1900	613	18.5	1.95	13
Comp 18-25	531000	14.2	2320	490	32000	13.3	2730	1200	16.2	5.02	25.7
Comp 26-31	625000	16.5	2640	560	24200	32	2930	1030	59.2	6.54	33
Comp 32-37	669000	16.3	2650	560	33200	32.1	2940	1180	58	6.65	32.5

Table 3. Summary of Metal Precipitate (MP) Process Removal Efficiency for Pb

ID	Pre-MP Filtrate (mg/L)	Post-MP Filtrate (mg/L)	Removal Efficiency %
Run 1	248	9.54	96.15
Run 2	254	5.51	97.83
Run 3	287	5.29	98.16
Run 6	355	7.98	97.75
Run 8	439	8.43	98.08
Run10	359	24.3	93.23
Run 13	396	10.2	97.42
Run 22	550	4.11	99.25
Run 30	206	9.71	95.29
Run 34	203	1.73	99.15
Run 35	263	1.46	99.44

The effectiveness of the metal precipitation process was based on the removal efficiency of Pb from the filtrate stream. Samples of filtrate pre- and post-metal precipitation were collected at intervals during specified test runs, and analysed for Pb. The results of the tests are presented in Table 3.

Substantial concentrations of Pb were measured in the filtrate stream prior to the metal precipitation process, whereas the post precipitation filtrate stream was typically <10 mg/L of Pb. Removal efficiencies were calculated, and all measured runs exceeded 93%.

Effectiveness of Polishing Filters

A series of two filters were used to polish the post metal precipitation brine stream. The first filter was a cartridge filter capable of removing colloidal sized particles, followed by an activated carbon filter to remove residual trace metals. The data from analysis on composite samples are presented in Table 4.

Table 4. Pre and Post Activated Carbon Filter Pb Concentrations in Post Metal Precipitation Filtrate

Sample	Pre-Filter (mg/L)	Post-Filter (mg/L)
Comp. 1	8.95	4.03
Comp. 2	6.37	3.93
Comp. 3	5.55	4.59

The data indicate that the filters act to further polish the brine filtrate from the metal precipitation process. These filters would be standard on any full-scale APEX

Treatment System to further enhance the capture of trace metals remaining in the post-precipitate filtrate stream.

Evaporative Concentration of Brine Stream

At the time of printing, the data from the evaporative tests on the polished brine stream had yet to be received from the laboratory.

CONCLUSIONS AND RECOMMENDATIONS

The demonstration program proved to be an overall success, in that the equipment proved to work to given specifications, and by-products generated from the APEX Treatment System meet targeted standards set prior to the test program.

Results from the Ontario Regulation 347 Leach Procedure on the treated filter cake indicate that the treated filter cake would be defined as a registered waste which could be disposed in a conventional sanitary landfill. A significant proportion of the results indicated that it is possible to generate an unregistered waste using the treatment process, however, there are cost implications involved, primarily, increased rinse volumes.

Chemical analysis of the pre- and post-metal precipitate filtrate stream indicate that the proprietary metal precipitation process is highly effective at removing the solubilised trace metals (especially Pb > 93% removal)

from the brine filtrate stream without the use of expensive chemical or flocculating reagents. The process consistently generated precipitates which contained about 64% Pb by weight.

In summary, the collective data provide a very positive indication that full-scale implementation of the APEX Treatment System is technically feasible.

REFERENCES

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ABSTRACT

A pilot study was conducted to evaluate the feasibility of a process for the treatment of municipal solid waste (MSW) incinerator bottom ash. The process involves the sequential extraction of metals from the ash using a series of reagents. The results of the study are presented in this paper. The process was found to be effective in removing a wide range of metals from the ash, including lead, cadmium, and copper. The process is simple and easy to operate, and it can be used to treat large quantities of ash. The results of the study indicate that the process is a promising method for the treatment of MSW incinerator bottom ash.

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