

Chemical and Mineralogical Transformations of Coal Fly Ash after Landfilling

Muluken B. Yeheyis, Julie Q. Shang and Ernest K. Yanful

Department of Civil and Environmental Engineering, The University of Western Ontario, London, Canada.

KEYWORDS: coal fly ash, characterization, weathering, acid neutralization capacity, leaching

ABSTRACT

Most applications of coal fly ash, such as concrete, structural fill, and waste stabilization, use fresh fly ash received directly from coal fired power generation plants. However, if the current rate of usage continues, the demand for fresh coal fly ash for various applications will increase and utilization of coal fly ash disposed in landfills will have to be considered. This study investigates the chemical, mineralogical and geochemical properties of coal fly ash disposed in a landfill for various durations and at various depths. The coal fly ash studied was from the Atikokan generation station in Northern Ontario, Canada. The effects of weathering/ageing on the disposed coal fly ash are studied in comparison with the fresh fly ash from the same site. The physical, mineralogical and micro-structural characterization results showed the alteration in mineralogy and microstructure of the fly ash, and revealed the formation of secondary minerals mainly due to hydration, carbonation and pozzolanic reactions that occurred after landfilling. The formation of secondary minerals during weathering of disposed fly ash samples has significant effect on acid neutralization capacity and leaching behavior of their components.

INTRODUCTION

Coal fly ash is a by-product of coal combustion in thermal power generating stations. It is composed mainly of silt-sized spherical amorphous ferro-aluminosilicate minerals and is generally characterized by low permeability, low bulk density, and high specific surface area.¹ Although coal fly ash is considered waste by itself, it has become a valuable by-product in numerous environmental and commercial applications due to its pozzolanic, cementitious and alkaline properties. These include its use as raw material in cement production, as an admixture in blended cements and as replacement for cement or as a mineral admixture in concrete; for agriculture to improve soil structure and water-holding capacity, as a liming agent to neutralize acidic soils, and as essential source of micronutrients for agricultural crops.^{2,3,4}

About 19% of the electricity generated in Canada is produced by coal burning power plants. Coal power production in Canada consumes roughly 93% of Canadian coal resource and produces approximately 5 million tonnes of coal fly ash annually.⁵ The statistics on the production and utilization of coal fly ash for the years 1999 through 2004 in Canada is presented in Fig. 1. In spite of the fact that the coal fly ash production currently outweighs its consumption in Canada, future utilization of coal fly ash is expected to grow due to growing innovative methods of utilization.

Most applications use fresh ash received directly from the power generation plants. However, if the current trends of increasing demand for fresh coal fly ash for various applications continue, utilization of disposed coal fly ash from landfill needs to be considered. In addition to the current high rate of utilization of fly ash, there is also a plan in discussion to phase out the burning of coal for electricity production in Canada (e.g. in Ontario by 2014) because of environmental concerns, which will further increase the need to use disposed fly ash.⁶ The main purpose of this study is to find out whether disposed coal fly ash from landfill has suitable engineering and environmental properties needed for various applications. In particular, this study is designed to perform a detailed characterization of fresh and disposed coal fly ash, and evaluate the effect of ageing/weathering on the chemical and mineralogical properties of the coal fly ash after it is disposed in the landfill.

MATERIALS AND EXPERIMENTAL METHODS

Materials

The fly ash samples used in this study were obtained from Atikokan thermal generating station, located in northwestern Ontario. Two types of Atikokan coal fly ash were used: fresh fly ash (FFA here after) collected directly from the precipitators, and disposed fly ash (DFA here after) collected from the landfill located near the Atikokan power generating station. Part of the ash landfill is capped with a geomembrane-soil cover system. The uncapped portion of the disposed fly ash has been continuously subjected to weathering and other natural processes. Three disposed fly ash samples, labeled as DFA-I, DFA-II and DFA-III, were collected from a borehole drilled in the uncapped area

of the landfill. The three samples were collected at different depths in the borehole to assess the spatial variability in geochemical and mineralogical properties of the disposed fly ash. DFA-I was taken near the surface, and DFA-II and DFA-III were taken from ~1-2 m and ~2-3 m below the surface, respectively. The disposed ash samples were air-dried in the laboratory, and the conglomerated ash particles were broken apart by using a rubber pestle and mortar.

Experimental Methods

The chemical and mineralogical properties of coal fly ash influence the engineering properties as well as the environmental impacts that may arise out of their use. Therefore, the elemental composition, mineral phases and microstructure of fresh Atikokan fly ash as well as possible changes that took place after landfilling were investigated. The chemical composition (major oxides and trace elements) of fresh and disposed fly ash samples was determined using x-ray fluorescence spectrometry (XRF), and inductively coupled plasma atomic emission spectrometry (ICP-AES). The mineralogical characterization of the fly ash samples was carried out by x-ray diffraction (XRD) using a Rigaku diffractometer, with Co-K α radiation (45kV, 160 mA) at scanning speed of 10° 2 θ /min. The mineralogical phases identified by XRD were confirmed by scanning electronmicroscopy (Hitachi S2600N SEM), and also by simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis over a temperature range of 30-1000 °C.

In order to gain a better understanding of the effects of chemical and mineralogical transformations that occurred in disposed fly ash and the environmental impacts of their utilization, the acid neutralization capacity and solubility characteristics of various chemical species associated with fly ash materials were examined using the generalized acid neutralization capacity test (GANC).⁷ The GANC test is based on a modified version of the acid neutralization capacity test (ANC)⁸ combined with the toxicity characteristic leaching procedure (TCLP).⁹ Each of the fly ash samples studied was divided into a batch of 16 sub-samples of 4 g in mass. Each sub-sample was placed into a centrifuge tube and 80 mL of leachant was added to the samples. The leachant was made from de-ionized water and 2 N acetic acid, with increasing acid concentration ranging from 0 to 6 equivalents per kilogram of dry fly ash. The bottles were tightly capped, placed on a rotary shaker and shaken at a speed of 28 rpm at room temperature for 18 hours, to ensure complete reaction between the acid solution and the fly ash samples. In order to compare the metal leaching results from the GANC test with the TCLP regulatory limits, 18 hrs of agitation time was used in this study instead of the 48 hrs prescribed in the original GANC procedure. Preliminary experiments revealed that 18 hrs of agitation were adequate for reaching the equilibrium pH. Since pH has been found to be the most important parameter influencing the leachability of heavy metals¹⁰, the metal leaching behavior of the fly ash samples under various pH conditions was assessed by filtering the remaining solution and analyzing the concentrations of heavy metal using ICP-AES.

RESULTS AND DISCUSSIONS

Mineralogical Transformations

The x-ray diffraction patterns of fresh and disposed fly ash samples are shown in Fig. 2. It can be observed from the figure that quartz and mullite are the most predominant minerals present in the FFA sample. The diffractograms of disposed fly ashes showed additional peaks at 29.4° , 36.0° , 39.4° , 43.2° , and 48.5° 2θ suggesting the presence of calcite, formed due to carbonation which occurred through the reaction of carbon dioxide present in the landfill with the alkaline material present in the fly ash. Ettringite was also detected in the disposed fly ash samples as shown by peaks at 9.08° and 15.78° 2θ . Essentially, the differences in the XRD patterns among the disposed fly ash samples were minimal. However, the XRD patterns of DFA-I revealed that carbonation process was predominant on the surface of the landfill. The amorphous phase of fresh ash (identified as a broad background hump from about 15 to 35° 2θ) has relatively shrunk in the disposed ash samples, suggesting possible weathering after disposal.

The thermogravimetric analysis (derivative weight loss) and differential scanning calorimetry (DSC) curves of fresh and disposed fly ashes are shown in Fig. 3. Changes in sample weight indicate material loss and phase changes that occur at particular temperatures. The total mass loss from FFA throughout the course of heating up to 1000°C the FFA is only 0.43% , indicating the absence of volatile minerals in the fly ash. In contrast, significant mass loss (more than 5%) was recorded in disposed fly ash samples as a result of dehydration (0°C to 200°C) and carbonate minerals decomposition (500°C to 800°C) of the secondary minerals formed during landfilling. DFA-I showed greater weight loss as a result of carbonate decomposition as compared to the disposed fly ash samples taken at deeper depths indicating the relative abundance of carbonate minerals (calcite) near the surface of the landfill.

SEM micrographs of fresh and disposed fly ash samples are presented in Fig. 4. A marked change can be observed in the surface morphology between the FFA and DFA samples. The FFA comprises smooth spherical particles, whereas the disposed fly ash samples are encrusted by secondary minerals and pozzolanic materials formed during landfilling. The differences in the surface morphology observed between the fresh and disposed fly ash samples are in agreement with the XRD results, which also showed the formation of secondary minerals in disposed fly ash as a result of weathering.

Bulk Chemical Analysis

The results of the bulk chemical analysis of the fly ash samples are presented in Table 1. As shown in the table, the main constituents of the fly ash samples are SiO_2 , Al_2O_3 , and Fe_2O_3 . The concentration sum of oxides (SiO_2 , Al_2O_3 , CaO , and Fe_2O_3) in the Atikokan fly ash is between 50 and 70 percent. Based on this, Atikokan fly ash would be classified as Class C fly ash according to the classification of the American Society for Testing and Materials Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete (ASTM

C 618). They also have relatively high CaO content (~12.34-16.41%). The trace element composition and concentration of fly ash mainly depends on the type of coal used, and the concentrations of minor elements are generally much higher in fly ash than in coal due to enrichment from the combustion process.¹¹ The major trace elements in both fresh and land filled ashes present with concentrations levels of environmental concern include As, Ba, Cu, Cr, Mn, Pb, Sr, V and Zn.

There was no significant difference in the elemental composition between the fresh and disposed fly ash as well as among disposed fly ash samples, indicating that the metals in the fly ash were immobilized in the landfill. Some of the constituents of the disposed fly ash samples may have changed to less soluble hydroxide and carbonate minerals due to weathering in the landfill (e.g. calcite, ettringite, and aluminosilicate minerals) as shown in the XRD analysis. These secondary minerals could have also prevented the leaching of metals from the disposed fly ash samples through adsorption, co-precipitation, and/or physical encapsulation. Trace metals such as Cu, Fe, Co, Mn, Mo, Ni, Pb, and Zn are co-precipitated with hydroxides of iron and aluminium, and neo-formed clay minerals in weathered municipal solid waste incineration (MSWI) bottom ash.¹² The cementitious and precipitated minerals could also serve as a physical barrier to the constituents of the disposed fly ash by clogging the pores of disposed fly ash and hence prevent their mobilization. The major difference in the loss on ignition between fresh and disposed ash samples is largely attributed to hydrated water and CO₂ loss from secondary minerals formed in the disposed fly ash samples after disposal (as shown in the thermogravimetric analysis).

Generalized Acid Neutralization Capacity Test

The acid neutralization behavior of the fresh and disposed fly ash samples is evaluated by plotting the pH of each extract as a function of equivalents of acid added per gram of dry solid (Fig. 5). The fresh fly ash showed very high alkalinity during the early stages (at lower acid addition), having a pH of 11.5 with only distilled water added. The pH of disposed ash samples with zero acid added was relatively lower than that of the fresh fly ash, which is mainly due to the fact that soluble basic oxides and hydroxides (e.g. CaO, MgO, Na₂O) have been depleted as a result of leaching and weathering in the landfill. However, the disposed ash samples show a high buffering capacity at near neutral pH (pH = 6.5 to 8), possibly due to the newly formed minerals after landfilling. Comparing the disposed fly ash samples, the sample taken near the surface of the bore hole (DFA-I) showed lower alkalinity at the early stages and high buffering capacity as more and more acid was added.

The concentrations of regulated elements from the GANC test are plotted as a function of the extract final pH (Fig. 6). In general, the solubility of the metals increased as the solution pH decreased. The concentrations of metals from disposed fly ash are found to be generally lower than those from the fresh fly ash, possibly due to the strong resistance to acid addition as observed from the ANC curves, which could buffer and maintain the pH of the leaching system at a level that the solubility of most metal oxides and hydroxides is minimal. The formation of less soluble species of these elements as

observed from their mineralogical analysis could also attributed to the low release in many of the elements from the disposed fly ash samples. None of the metal concentrations leached from either fresh or disposed ash samples exceeded the allowable maximum concentrations specified by TCLP and Ontario Regulation 558 Leachate criteria. Therefore, it can be concluded that both fresh and disposed fly ashes are not hazardous with respect to toxic metals and can be recycled without adverse environmental impact.

CONCLUSIONS

In this study, a comprehensive characterization of Atikokan fresh and disposed fly ash samples was performed from the standpoint of utilizing the materials for environmental applications. Physical, mineralogical and micro-structural characterization results revealed significant differences between fresh and disposed fly ash samples. XRD, TGA, and SEM analysis results showed the alteration in mineralogy and microstructure of the fly ash after disposal and confirmed calcite was the predominant secondary mineral formed in the disposed fly ash samples. Despite the chemical and mineralogical transformations and slight variations in chemical compositions of disposed fly ashes, the overall results of this study suggest both fresh and disposed materials have favorable engineering properties that make them suitable for re-utilization.

ACKNOWLEDGEMENTS

The authors acknowledge funding for the study provided by the Natural Sciences and Engineering Research Council of Canada (NSERC) under its Collaborative Research and Development Project Grant (No. CRDPJ 319808-04), Goldcorp Musselwhite Mine, Ontario Power Generation-Atikokan Generating Station and Golder Associates.

REFERENCES

- [1] Petrik, L., Hendricks, N., Ellendt, A. and Burgers, C. 2007. Toxic element removal from water using zeolite adsorbents made from solid waste residues. Water Research Commission, WRC Report No. 1546/1/07, University of the Western Cape, South Africa.
- [2] Adriano, D.C., Page, A.L., Chang, A.C., and Elseewi, A.A. 1982. Cadmium availability to sudan grass grown on soils amended with sewage sludge and fly ash. *Journal of Environmental Quality*, 1:197-203.
- [3] Conn, R. E., Sellakumar, K., and Bland, A. E. 1999. Utilization of CFB Fly Ash for Construction Applications. *Proceedings of the 15th International Conference on Fluidized Bed Combustion*, May 16 - 19, 1999, Savannah, Georgia, ASME, 19p.
- [4] Vincini, M., Carini, F. and Silva, S. 1994. Use of alkaline fly ash as an amendment for swine manure. *Bioresource Technology*, 49:213-222.
- [5] Natural Resources Canada. 2004. Canadian Mineral Year Book. Available on-line at http://www.nrcan.gc.ca/mms/cmy/pref_e.htm [accessed April 30 2007].
- [6] OME. 2007. Ontario Ministry of Energy. Available on-line at <http://www.energy.gov.on.ca/index.cfm?fuseaction=english.electricity> [accessed March 1 2007].
- [7] Isenburg, J.E. and Moore, M. 1992. Generalised acid neutralisation capacity test. *Stabilization and Solidification of Hazardous, Radioactive and Mixed Waste*, In: T.M. Gilliam and C.C. Wiles (Eds.), STP 1123, American Society for Testing and Materials, Philadelphia, PA, USA, pp 361-377.
- [8] Environment Canada and Alberta Environmental Center. 1986. Test Methods for Solidified Waste Characterization Acid Neutralization Capacity (ANC), Method No. 7, Edmonton, Canada.
- [9] U.S. EPA. 1992. Method 1311: Toxicity Characteristic Leaching Procedure. *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW846)*, available on-line at <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/1311.pdf> [accessed May 25 July 2007].
- [10] Cote, P.L. and Constable, T. 1982. Evaluation of Experimental Conditions in Batch Leaching Procedures. *Resources and Conservation*, Elsevier Scientific Publishing Company, Amsterdam, Netherlands.
- [11] Lindsay, A.L. 1979. *Chemical equilibria in soils*. John Wiley & Sons, New York.
- [12] Zevenbergen, C., Bradley, J. P., Van Reeuwijk, L. P., Shyam, A. K., Hjelmar, O., and Comans, R. N. 1999. Clay formation and metal fixation during weathering of coal fly ash. *Environmental Science and Technology*, 33: 3405-3409.

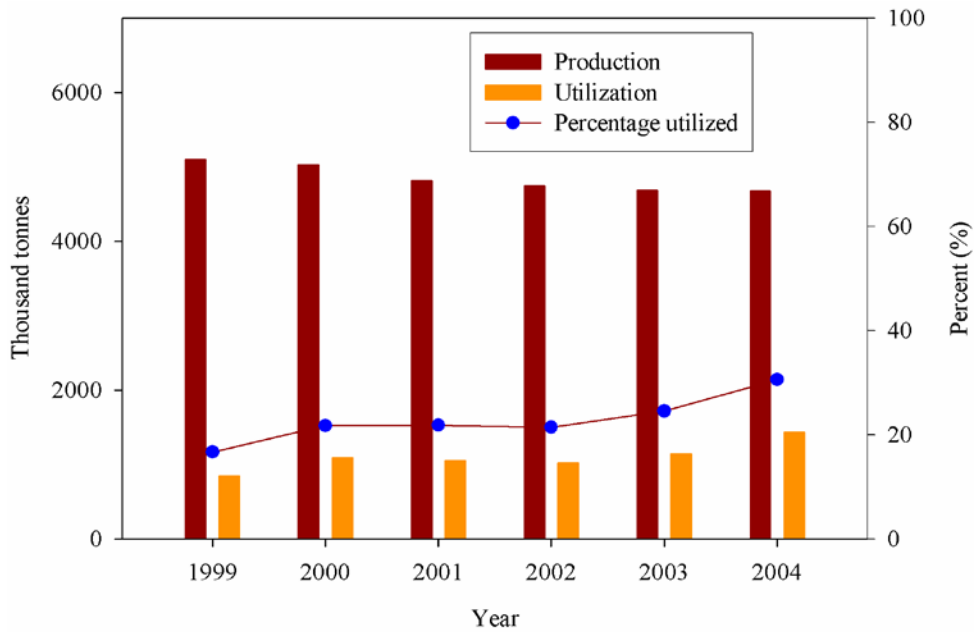


Fig. 1. Historical coal fly ash production and utilization in Canada, 1999-2004 (Natural Resource Canada)

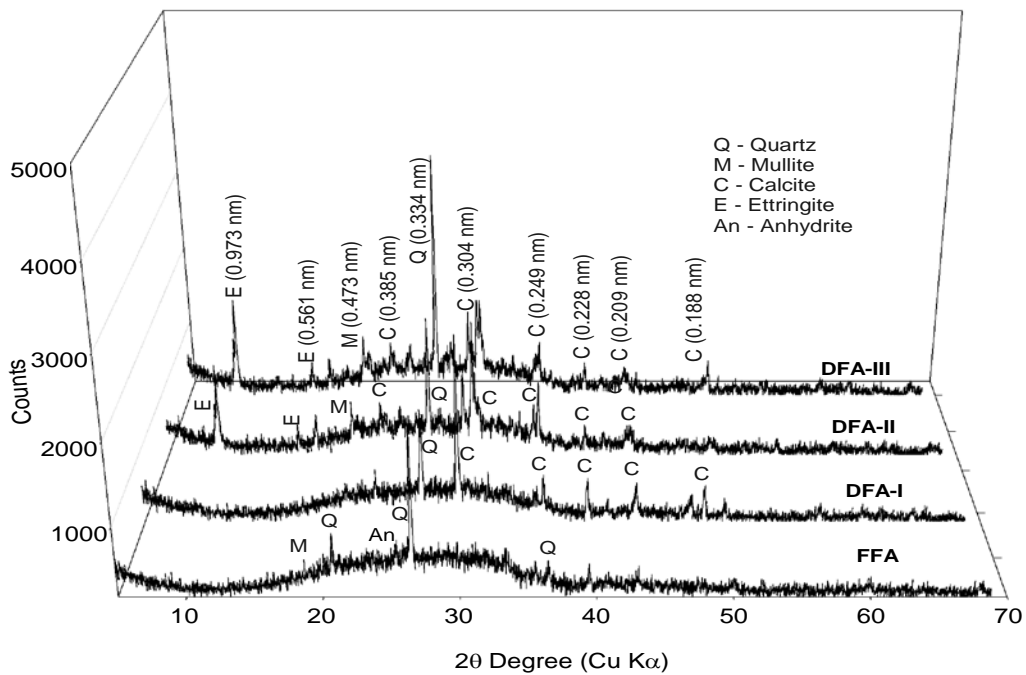


Fig. 2. X-ray diffractograms of fresh and disposed fly ash samples.

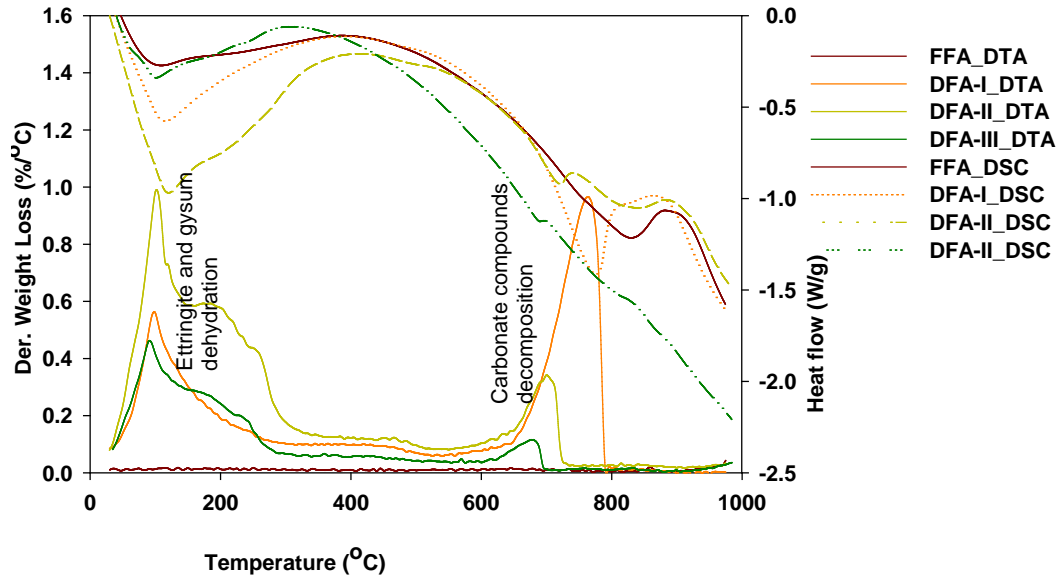


Fig. 3. Thermal analysis of fresh and disposed fly ash samples.

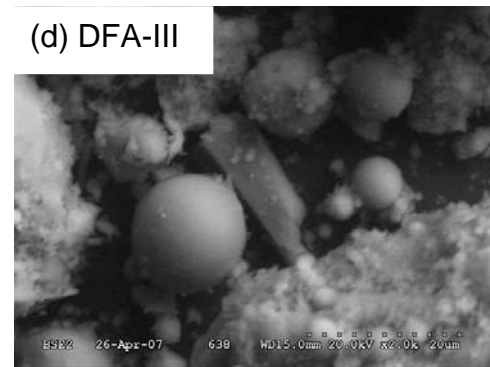
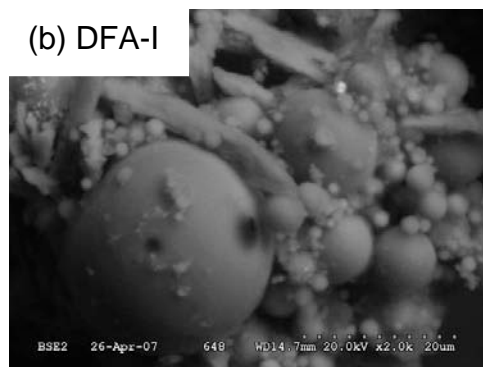
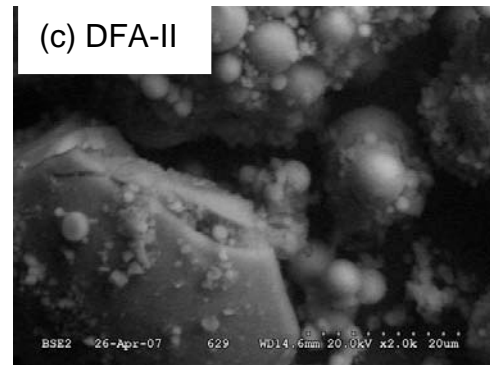
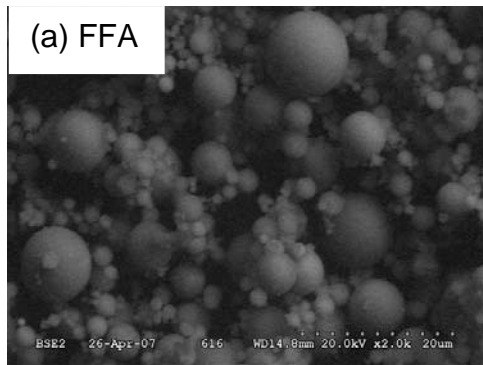


Fig. 4. SEM Images of fly ash samples (x2000). (a) fresh fly ash showing smooth surfaces of fly ash particles, and (b) – (d) disposed fly ash materials showing cementation and formation of secondary minerals.

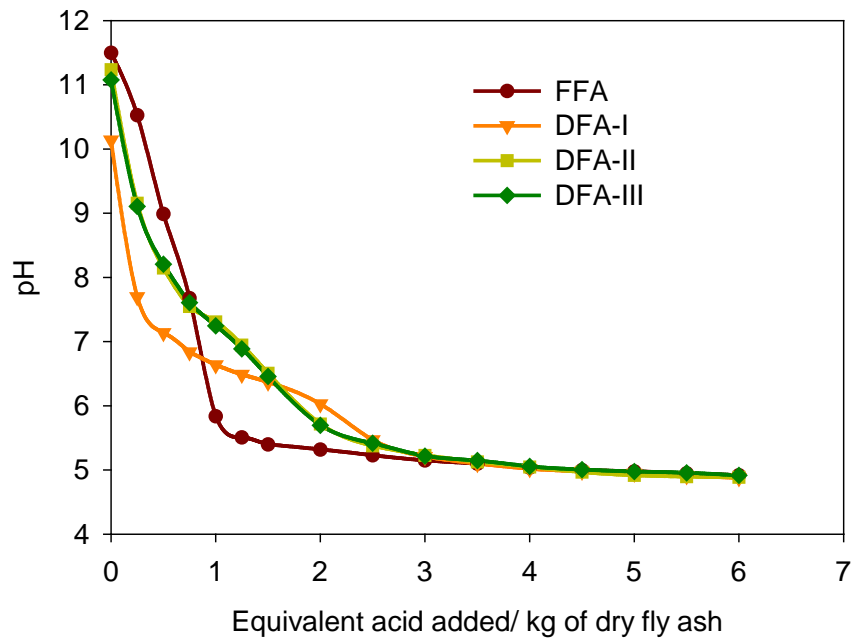
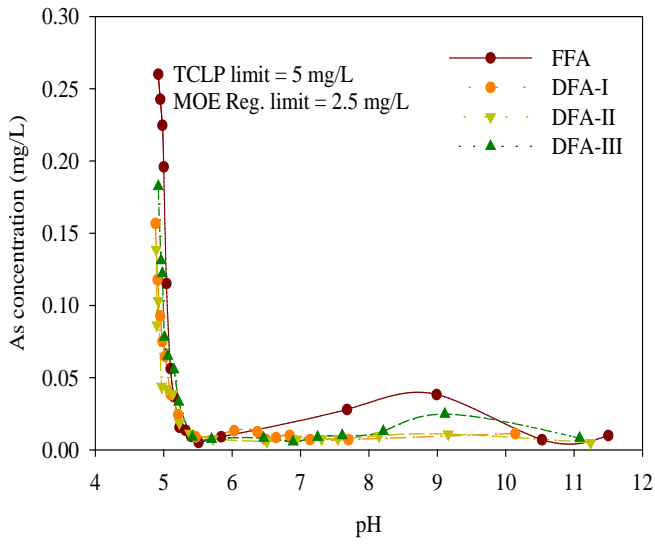
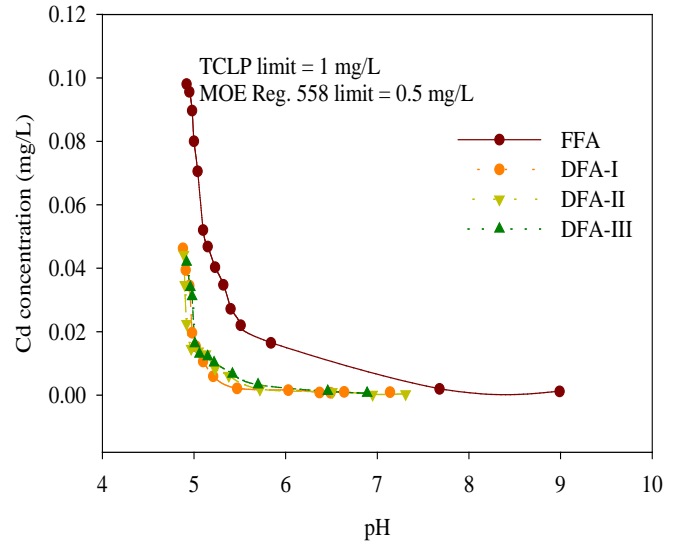


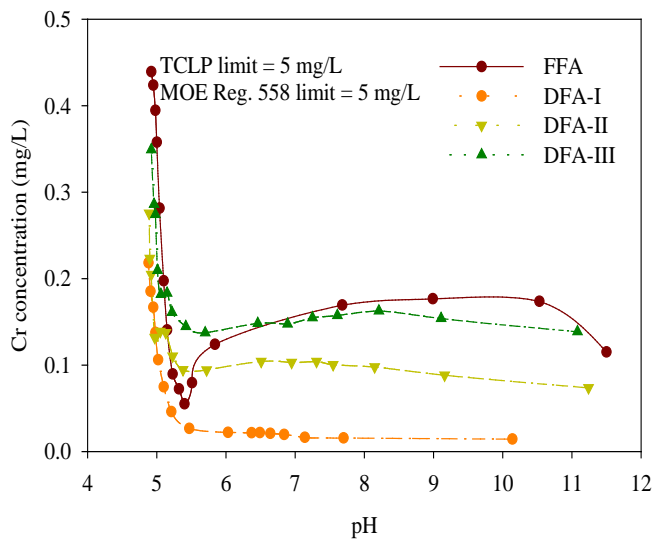
Fig. 5. Acid neutralization behaviors of fresh and disposed fly ash samples.



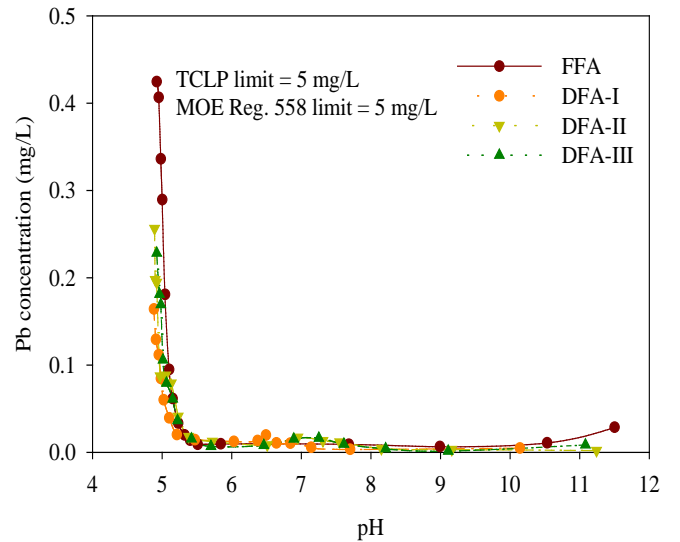
(a) As



(b) Cd



(c) Cr



(d) Pb

Fig. 6. Concentrations of selected heavy metals from GANC test (a) As; (b) Cd; (c) Cr; and (d) Pb.

Table 1. Chemical composition of Atikokan fresh and disposed fly ashes

Element/Compound	FFA	Disposed Fly Ashes		
		DFA-I	DFA-II	DFA-III
<u>Major Oxides (%)</u>				
SiO ₂	41.50	40.58	39.81	40.87
Al ₂ O ₃	18.91	18.18	18.83	18.21
Fe ₂ O ₃	6.31	5.03	4.70	4.3
TiO ₂	0.71	0.70	0.77	0.77
K ₂ O	0.86	0.89	0.62	0.77
MgO	3.66	3.03	2.78	2.70
CaO	16.41	15.01	13.68	12.34
MnO	0.03	0.03	0.03	0.03
Na ₂ O	9.12	6.81	6.70	6.34
P ₂ O ₅	0.41	0.41	0.48	0.29
SO ₃	1.05	0.52	1.02	1.63
BaO	0.96	0.98	0.94	0.84
L.O.I.	0.40	7.21	8.38	9.62
Total	95.32	99.38	98.74	98.71
<u>Trace elements (mg/kg)</u>				
As	44.2	53.7	24.6	9.1
Ba	8570	7970	7120	6380
B	1800	1790	1570	1700
Cd	8.2	6.2	5.6	6.6
Cr	32.6	30.1	28.5	32.9
Co	5.09	8.2	5.9	6.5
Cu	39.0	46.0	46.0	48.5
Pb	110	26.1	25.4	12.2
Mn	158	175	168	134
Mo	27.0	15.9	8.9	26.4
Ni	23.5	12.4	18.1	13.2
Sr	1130	4300	3460	3250
V	110	81.7	67.3	79.8
Zn	46.7	37.1	32.3	38.5