

Leachability of Trace Metal Elements from Fly Ashes, and from Concrete Incorporating Fly Ashes

by M. H. Zhang, M. C. Blanchette, and V. M. Malhotra

Synopsis:--This paper presents information on the leachability of trace metal elements from a number of fly ashes from Canadian and the U.S. sources, and from the concrete incorporating the fly ashes.

The concentrations of all regulated elements Ag, As, B, Ba, Cd, Cr, Cu, Hg, Pb, and Se in the leachates from the nine fly ashes tested were within the limits of the United States Environment Protection Agency and the Transportation of Dangerous Goods Act Regulations of Canada. The leaching of As, B, Ni, and Se from the fly ashes appeared to increase with an increase in their content in the fly ash; however, there were some exceptions. In general, the concentration of As leached from the fly ashes derived from the bituminous coals was much higher than that from the lignite or sub-bituminous coals.

Regardless of the type and percentage of the fly ash used, w/cm of the concrete, and curing condition, none of the trace metals in the leachates from the fly ash concrete samples exceeded the regulated concentration limits by the United States Environment Protection Agency and the Transportation of Dangerous Goods Act regulations of Canada. The concrete incorporating the fly ashes is, therefore, considered environmentally stable.

Keywords: concrete; fly ash; leachability; trace metals

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INTRODUCTION

Portland cement concrete is and will remain a major construction material of choice. Unfortunately, the production of portland cement, the most important component of concrete, is very energy intensive. Furthermore, the manufacturing of portland cement is environmentally unfriendly because for each tonne of cement produced, approximately one tonne of CO_2 is released into the atmosphere. Thus, replacing part of portland cement by mineral by-products such as fly ash or ground, granulated blast-furnace slag in concrete can contribute significantly to the reduction of CO_2 emissions, and savings in energy.

There is a growing concern that the emissions of CO_2 and other greenhouse gases are affecting adversely the global climate. It is, therefore, imperative that policies and programs be developed to reduce the level of CO_2 emissions. The Canadian Government has announced that Canada, in accordance with the Kyoto Protocol, will reduce CO_2 emissions to about 6% below 1990 level by the year 2010. By replacing portland cement in concrete with fly ash, a by-product from the burning of coal in electric utilities, CO_2 emissions can be reduced considerably that can help to meet the above objective. Typical replacement levels of fly ash in portland cement concrete are about 20% by mass of the total cementitious materials. With increasing use of fly ash in concrete, questions have been raised as to the potential contamination of the surface and ground water by the trace elements in fly ash as a result of the leaching.

This paper presents information on the leachability of trace elements from a number of fly ashes from Canadian and the U.S. sources, and from the concrete incorporating the fly ashes determined according to the United States Environment Protection Agency (EPA) regulatory method 1311 - Toxicity Characteristic Leaching Procedure (TCLP). The effects of fly ash source and content, w/cm, and curing conditions of the concrete on the leachability of trace metal elements were also evaluated. This study provides data that are not available in published literature. The effects of leaching conditions that simulate wetting and drying and the types of leachants on the leachability of trace metal elements have been discussed elsewhere [1,2].

LITERATURE REVIEW

Published data have shown that the leachability of trace elements from a fly ash is dependent on the chemical composition of the fly ash, a function of the operating conditions of thermal power plants [3], and the exposure conditions. The combustion temperatures of the boiler and the operating temperatures of the emission control devices are significant controlling parameters affecting the distribution of the trace elements in a coal ash. In most cases, for different coals burned in the same combustion unit under similar operating conditions, the distribution of most chemical species are similar [3]; however, for different coals burned under different combustion conditions, no definite distribution pattern of trace elements can be determined. Incomplete combustion can result in higher concentration of leachable trace elements in a coal ash; and a coal with a lower heat content yields more leachable trace elements, probably because of the lower combustion temperatures inside the furnace [3].

De Groot et al. [4] investigated the leaching characteristics of selected trace elements such as arsenic (As), cadmium (Cd), copper (Cu), antimony (Sb), selenium (Se), molybdenum (Mo), lead (Pb), tungsten (W), vanadium (V), and zinc (Zn) from coal fly ashes as a function of the acidity of the leachant* and the liquid/solid. The test consisted of three parts: a column-leaching test, a serial batch-leaching test, and a test for determining the maximum leachability. Fifty fly ashes from a wide variety of sources were analysed, and only five fly ashes were tested using all the three tests. The authors found that with respect to leaching, differences in elemental composition of the fly ashes are far less important than the differences in the pH of the leachant. The pH level of a leachant is the controlling factor in the leachability of trace elements from a fly ash, and at a high pH (>11) the solubility of trace elements is limited. All the ashes tested showed common leaching characteristics for several groups of elements. The trace elements present in the form of species, e.g. As, Sb, Se, Mo, W, and V, behave similarly, and showed a characteristic

* Leachant is defined as a solution or liquid used for leaching.

maximum leaching at neutral pH, and decrease in leaching towards lower and higher pH values. De Groot et al. [4] also found that the length of the batch-leaching test of 24-hour duration is sufficient for most elements to reach equilibrium, and can be a significant factor only for a few elements such as arsenic, Sb, and V at highly alkaline conditions and low liquid/solid for which the reaction kinetics are slow.

The leaching characteristics of the fly ashes from the thermal power plants operated by Ontario Hydro, Toronto, Canada have been documented in a review report [5]. Fly ashes derived from bituminous coals generally have higher content of the trace metal elements (As, Se, Cr, V, and Ti) than the fly ashes from lignite coals. The concentration of trace elements extracted from leachates* of the fly ashes were less than 10 times the criteria outlined in Schedule 4 of Ontario Ministry of Environment Regulation 309 (drinking-water standard).

The leaching of trace elements from concrete and mortars incorporating a fly ash as partial cement replacement was investigated by Van der Sloot, de Groot, and Hoede [6]. Fly ashes from conventional installations and installations operating with low NO_x burners were included in the study, and cement replacement levels in concrete ranged from 20 to 40%. Both portland cement and blast-furnace slag cements were used in the study, and the water-to-cementitious materials ratio (w/cm) of the concrete ranged from 0.50 to 0.64. The leaching of the concrete was determined using a modified procedure based on Dutch standard NEN 7345. The mortar specimens were crushed in a jaw-crusher, and separated into three fractions (A: 1.5-6 mm, B: 0.5-1.5 mm, and C: <0.5 mm). These samples were then treated with demineralized water with different liquid-to-solid ratios (500, 100, 20, 4, 1), and the contact times were 0.5, 5, and 50 hours. After the treatment, the pH and the concentration of the elements As, Br, Cr, Cu, Ga, Mo, Sb, Sr, W, Zn, Ca, Si, Mg, Na, K, Cl, F were determined. The results indicated that the concentration of these elements in the leachate from the fly ash concrete was higher than that from the control portland cement concrete. Nevertheless, with the exception of Mo, the leaching of the above elements from the fly ash concrete was generally within the specification of the Building Materials Decree of the Netherlands. This implies that replacing part of portland cement by fly ash is environmentally acceptable.

Hohberg and Schiessl [7] studied the effect of the type of cement and fly ash, w/cm, and curing age on the leaching behaviour of the mortars and concrete. Both normal portland cement and blast-furnace slag cement were used in the investigation. Four fly ashes with different heavy metal contents were selected for the evaluation. The fly ash content was 20% by mass of (Cement + 0.5 Fly Ash), and the W/(C+0.5FA) of the mortars ranged from 0.4 to 0.6, and the W/(C+0.5FA) of the concrete was 0.5. A number of 40 x 40 x 160-mm prisms and 100-mm cubes were made from the mortar and concrete mixtures, respectively. After one day in the

*Leachate is defined as a solution obtained by leaching.

moulds, the specimens were cured in a chamber at 20 °C and 95% relative humidity until the ages of 90, 180, and 360 days for leaching tests. Tank-leaching tests similar to that described in Dutch Standard NEN 7345 with a duration of 56 days, and 8 leachant renewals were performed with the mortar and concrete specimens. The results indicated that the leaching of the metal elements (As, Cd, Cr, Cu, Pb, Ni, and Zn) from mortars and concrete with and without fly ash was generally very low, and was largely independent of the total amount of the fly ash incorporated. The incorporation of the fly ash in concrete reduced the leaching rate in case of most trace elements especially zinc. The w/cm had no distinct influence on the leachability of the metal elements, and longer curing led to lower leaching rates.

SCOPE

The leachability of trace elements from seven fly ashes from the Canadian sources and two fly ashes from the U.S. sources, and from the concrete incorporating the fly ashes is presented. In these nine fly ashes, seven of them meet the requirements of ASTM Class F fly ash, one of them meets the requirements of ASTM Class C fly ash, and the remaining one meets all the requirements of ASTM Class F ash except for the fineness. The fly ash content in concrete ranged from 10 to 60% by mass of the total cementitious materials, and the w/cm of the concrete ranged from 0.40 to 0.70. The concrete was cured under the following three conditions prior to the leaching tests: (1), 1-day moist curing and 27-day air drying to simulate the field practice, (2), 7-day moist curing and 21-day air drying to simulate the condition most often specified but rarely followed in the fields, and (3), 28-day moist curing to simulate an ideal laboratory-curing condition.

All the fly ash and concrete samples were tested according to EPA method 1311 - Toxicity characteristic leaching procedure (TCLP)*, using a 0.1 N acetic acid leachant with a pH of 2.88.

MATERIALS

Fly Ashes

Seven fly ashes from locations across Canada were selected for this study, and they were Point Tupper, Nova Scotia; Lingan, Nova Scotia; Belledune, New Brunswick; Thunder Bay, Ontario; Sundance, Alberta; Forestburg, Alberta; Genesee,

*United States Environmental Protection Agency (1990) "Toxicity characteristic leaching procedure, method 1131". In Test Methods for Evaluating Solid Waste, EPA SW-846 (Revision 0, November 1990).

Alberta. Two fly ashes from Belews Creek, Georgia and Coal Creek, North Carolina in the United States were also included in the study.

The physical properties and chemical composition of major elements, as well as the content of trace elements of the fly ashes were determined, and the results are summarized in Tables 1 and 2, respectively. The data on the trace elements in coal ash, in cement and in soils are also in Table 2 for comparison purposes (8,9).

For the nine fly ashes evaluated, seven of them met the requirements of ASTM Class F ash, and one of them (Thunder Bay ash) met the requirements of ASTM Class C ash. However, one fly ash (Genesee) met all except the fineness requirement of ASTM Class F ash.

Cement

ASTM Type I portland cement was used for making concrete. Its physical properties and chemical composition are given in Table 3.

Aggregate

The coarse aggregate used was a crushed granite with a maximum nominal size of 19 mm, and the fine aggregate was natural sand from the Ottawa region. Both the coarse and fine aggregates were separated into different size fractions and recombined to a specified gradation shown in Table 4. The specific gravities of the coarse and fine aggregates were 2.72 and 2.70, respectively; the corresponding values for water absorption were 0.5 and 0.8 percent, respectively.

Superplasticizer

A sulfonated, naphthalene formaldehyde-condensate type superplasticizer was used in some of the concrete mixtures. The superplasticizer is a dark brown solution containing 42 percent solids.

Air-Entraining Admixture

A multi-component synthetic-resin type of air-entraining admixture was used in all the concrete mixtures.

CONCRETE MIXTURES

Mixture Proportions

Twenty concrete mixtures were prepared, and 102 x 203-mm cylinders were made for compressive strength and leaching tests. The mixture proportions of the concrete are given in Table 5. A control portland cement concrete with a w/c of 0.5 was used as the reference. Nine fly ashes were evaluated. The Lingan fly ash was selected for evaluating the effects of the percentage of fly ash and w/cm on concrete leaching because it has the highest As content of the nine fly ashes. The fly ash content ranged from 10 to 60% by mass of the total cementitious material. The w/cm ranged from 0.40 to 0.70. Two high-volume fly ash concrete mixtures with a low w/cm of 0.32 were also included for evaluation.

CASTING AND CURING OF CONCRETE SPECIMENS

The concrete was mixed in a laboratory counter-current mixer for a total of 5 minutes. The properties of fresh concrete including the slump, air content, and unit weight were determined immediately after the mixing had been completed.

A number of 102 x 203-mm cylinders were cast from each mixture for determining the compressive strength, and the leachability of metals from concrete. The cylinders were cast in two layers and consolidated on a vibrating table.

After casting, all the cylinders were left covered with wet burlap in the casting room for approximately 24 hours, then demolded and transferred to a moist-curing room at $23 \pm 2^\circ\text{C}$ and 100% relative humidity until required for testing. At the time of testing, the concrete cylinders were taken out of the moist-curing room either to be cured further in the laboratory air or to be prepared for testing.

The compressive strength of the concrete was determined after 7 and 28 days of moist curing. For various leaching tests, three different curing regimes were used in this study. Most of the cylinders were cured in a moist-curing room for 7 days followed by exposure to laboratory air for 21 days before the leaching tests to simulate the condition most often specified but rarely followed in the field. For selected concrete mixtures, additional cylinders were cured in the moist-curing room for one day followed by exposure to laboratory air for 27 days to simulate the field practice. In the third curing regime, the cylinders were cured in the moist-curing room for 28 days to simulate an ideal laboratory-curing condition.

PROPERTIES OF FRESH CONCRETE

The properties of the fresh concrete including the slump, unit weight, air content, and temperature are summarized in Table 6. The slump of the concrete ranged from 65 to 230 mm, and the air content ranged from 4.9 to 6.9%. The unit weight of the fresh concrete was $2350 \pm 57 \text{ kg/m}^3$, and the temperature of the fresh concrete ranged from 19 to 25°C.

COMPRESSIVE STRENGTH AND DENSITY OF CONCRETE

The density and compressive strength of the concrete cylinders at 7 and 28 days are given in Table 6. The control portland cement concrete had compressive strengths of 29.1 and 34.3 MPa at 7 and 28 days, respectively. The compressive strength of the concrete incorporating 30% fly ash but with the same w/cm as the control concrete ranged from 17.8 to 23.0 MPa at 7 days and 24.8 to 33.9 MPa at 28 days. The 28-day compressive strength of the concrete incorporating Lingan fly ash decreased from 35.0 to 15.3 MPa as the fly ash content increased from 10 to 60% by mass of the total cementitious materials. The density of the concrete determined at one day ranged from 2308 to 2444 kg/m³.

LEACHING TESTS

In general, a leaching test involves bringing a waste material in contact with a leachant to determine the components that will be dissolved from the waste. The purpose of leaching tests is to either classify a waste for disposal or to determine the leachate quality.

Leaching tests are divided into two broad categories depending on whether the leachant is renewed or not. For extraction tests (batch-leaching tests) the leachant is not renewed; instead a specific amount of waste is brought in contact with a specific amount of leachant for a specified time. At the end of the test, the liquid is separated from the waste and analyzed. These tests are short term, have good reproducibility, are simple to perform, and are often used to simulate the "worst case" scenario for leaching of the waste. All regulatory leaching protocols specify extraction tests.

Dynamic tests are those in which the leachant is continuously or intermittently renewed to maintain a constant driving force for leaching, e.g. column-leaching tests. The column-leaching test is performed by packing the material to be evaluated in a column, and passing a given volume of leachant through the material. This type of the test provides information about the kinetics of waste dissolution, and they are generally considered to be more representative of the field conditions.

In this study, the leachability of the fly ashes, and concrete incorporating the fly ashes was determined by the EPA TCLP test (18-hr extraction). The results on long-term batch-leaching test and column leaching tests have been reported elsewhere [1,2].

Leaching Test for Fly Ashes

The leachability of the fly ashes was determined according to the EPA (U.S.) Testing Method 1311 - Toxicity Characteristic Leaching Procedure (TCLP), that is a standard regulatory method for classifying materials as hazardous or non-hazardous. The material to be tested is crushed or ground to pass through a 9.5-mm sieve. The extraction fluid to be used depends on the pH of the material being tested. If the initial pH of a 5 gram-sample of the material mixed with 96.5 mL of distilled water is greater than 5.0, the waste is acidified with 3.5 mL of 1N HCl, heated for 2 minutes, cooled to room temperature, and then measured again for pH. If the pH of the resulting suspension is less than or equal to 5.0, a 0.1N sodium acetate buffer solution is used. If the pH is greater than 5.0, as in the cases of the fly ashes, a 0.1N acetic acid solution with a pH of 2.88 is added to the solid phase of the waste in a liquid-to-solid ratio of 20:1. The mixture is then agitated for 18 hours and the leachate is then filtered, and analyzed for Ag, As, B, Ba, Cd, Co, Cr, Cu, F, Fe, Hg, Mn, Ni, Pb, Se, Tl, U, V, Zn, and Zr. The TJA IRIS simultaneously inductively coupled plasma-atomic emission spectrometer (ICP-AES) was used to determine the concentration of B, Fe, Zn, and Zr. The VG PlasmaQuad inductively coupled plasma mass spectrometer (ICP-MS) was used to determine the concentration of Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Tl, U, and V. Fluorine was determined by the ion-selective electrode. Mercury was determined by the flow-injection cold vapour atomic absorption spectrometry.

Leaching Test for Concrete Incorporating Fly Ashes

The leachability of the trace elements from the concrete was determined using the same method as described above. After 28 days of curing, a slice of concrete, approximately 9.5-mm thick, was cut from the mid-height of a cylinder from selected concrete mixtures and curing regimes. A part of each slice weighing approximately 100 grams was crushed carefully using a hammer so that all particles were < 9.5 mm, and the variation in the particle-size distribution was not significant. The particle-size distribution of the samples can be found in reference [1].

Each crushed concrete sample was treated with an acetic acid solution of pH 2.88 at a liquid-to-solid ratio of 20:1 for a period of 18 hours. The leachate was filtered, and analyzed for pH, As, Cd, Cr, Cu, Pb, Ni, Se, Zn, and Fe. Quantitative elemental analyses of the leachates were performed by ICP-AES for Fe and Zn, and

by ICP-MS for As, Cd, Cr, Cu, Ni, Pb, and Se. These elements were selected by comparing the content and the leachability of the metals from fly ashes and portland cement shown in Tables 2 and 7, respectively.

WATER QUALITY GUIDELINES

Leaching tests determine whether the waste will release contaminants into an aqueous medium, and based on the dissolved concentrations from the tests, a material can be classified as hazardous or non-hazardous. The regulatory leach protocol, on which most other tests are based is the Environmental Protection Agency (EPA) Extraction Procedure Toxicity test (EP Tox) that was promulgated in the United States in 1980. The criteria for metals are set at 100 times the National Drinking Water Standards, and the materials from which leachates exceed these criteria are characterized as hazardous. In 1990, the U.S. EPA replaced the EP Tox test with the Toxic Characteristic Leaching Procedure (TCLP), that incorporates a number of procedural and equipment changes but leaves the criteria for the metals unchanged.

In Canada, the provinces have adopted leachate-extraction procedures that are similar to those of EP Tox. The only major difference is in the list of contaminants in the leachate that vary from one province to another. Those provinces that do not have hazardous waste regulations can utilize the provisions of the Transportation of Dangerous Goods Regulations (TDGR). The TDGR incorporated the Leachate Extraction Procedure CGSB 164-GP-1MP in 1989 in which list of contaminants and numerical criteria are identical to those used in Ontario.

Leachate-quality criteria for metals for the various tests discussed is given in Table 8.

RESULTS AND DISCUSSION

Leachability of Fly Ashes

The results of the leachability of the trace elements from the fly ashes are summarized in Table 7. The concentration of elements Ag, As, B, Ba, Cd, Cr, Cu, Hg, Pb, Se, and Zn in the leachates from all the fly ashes tested were within the limits mentioned above. Concentrations of Ag, B, Ba, Cd, Cu, Hg, Pb, and Zn are at least an order of magnitude below the limits set out in Table 8. The fly ashes are environmentally safe with respect to the TCLP regulatory test.

The arsenic (As) content in the leachates from the four fly ashes derived from the bituminous coals (Point Tupper, Lingan, Belledune, and Belews Creek) ranged from 0.850 to 1.317 ppm, and this was much higher than that of the fly ashes from lignite or sub-bituminous coals (<0.1 ppm). However, even the highest arsenic content in the leachate from Belledune fly ash was still well below the U.S. EPA and Canadian TDGR regulatory limits.

The chromium (Cr) content in the leachates from the fly ashes derived from the bituminous coals was ≤ 0.070 ppm; this was much lower than that of the fly ashes from lignite or sub-bituminous coals (0.164 - 0.661 ppm). The EPA and TDGR regulatory limit for the Cr is 5.0 ppm.

The selenium (Se) content of the leachates from most of the fly ashes was < 0.2 ppm except for that from the Belews Creek fly ash (0.55 ppm). The regulatory limit of the selenium specified by EPA of the U.S.A. and the province of Ontario, Quebec, and British Columbia in Canada is 1.0 ppm.

The leachability of As (except that from the Belews Creek fly ash), B, Ni, and Se from the fly ashes appeared to increase with an increase in its content in the fly ashes, while the leachability of Fe, Ba, Cd, Cr, Cu, Pb, and Zn did not appear to be related to their content in the fly ashes. Figure 1 illustrates the relationships between the concentrations of As, Cu, Ni, and Zn leached from the fly ashes and their content in the fly ashes.

Leachability of Metal Elements from Concrete

The effects of the fly ash source, fly ash content, w/cm, and curing time on the concentration of metals As, Cd, Cr, Cu, Fe, Ni, Pb, Se, and Zn in the leachates from the concrete is presented in Tables 9 to 12. The concentrations of the metal elements in the leachates were significantly lower than the limits specified by the EPA, U.S.A, and the TDGR, Canada.

The neutralizing potential of the concrete is underlined by the general rise in the pH over the 18- hour test procedure (final pH ranging from 5.3 to 6.5) relative to the pH of the leachant. Measured concentrations of Se were at or below the detection limits, and therefore, will not be discussed further. For Pb, many of the values were close to or below detection limit again making comparisons difficult. A summary of the observations of the leaching trends is presented in Table 13.

Effect of fly ash--In general, all the fly ash concrete samples showed similar or higher metal values when compared with the control portland cement concrete except for Cr. Chromium values for the fly ash concrete samples tested were similar to or lower than those of the control portland cement concrete.

Effect of the source of fly ash--For fly ash, the partitioning of trace metals between the spherical portion of the fly ash (glassy structure, relatively immune to dissolution) and the surface of the sphere (easily exchangeable or adsorbed molecules that are more prone to dissolution) will ultimately affect the nature of the produced leachate [10]. A comparison of As, Cu, Zn and Ni leached during the TCLP test versus the trace metal content in the nine fly ashes tested is presented in Fig. 1.

As shown in Fig. 1, the degree of leachability of As from a fly ash is reflected in the content of that metal in the fly ash itself. The same is true for the leachability of As from the fly ash concrete (Fig. 2). For example, concrete containing Point Tupper, Lingan, and Belledune fly ashes (Mixtures T1, T2, and T7) showed the highest concentrations of As in their leachates from the TCLP test; this is because the above fly ashes had the greatest content of As of 688, 980, and 505 ppm, respectively. Other metals analyzed did not show the same relationship.

For arsenic, the percentage leached from the concrete incorporating 60% Lingan fly ash (Mixture T14) of the total available metal in the mixture have been calculated, and summarized in Table 14. This concrete represents the highest arsenic content at ~80mg/kg concrete, and is considered as the extreme. The total concentration of arsenic leached from the concrete was less than 0.5% of the total available arsenic from the fly ash in the concrete.

An assessment of the partitioning of these elements between the glassy and surface portions of the fly ashes was not done in this study. However, in general As, Cd, Pb, and Zn have been reported to show surface enrichment, while data for Cr, Cu and Ni are reported to be inconclusive [10].

Effect of fly ash content--Figure 3 shows the effect of the percentage of Lingan fly ash in concrete on the concentrations of As, Cu, Ni, and Zn in the leachates from the concrete in the TCLP leaching test. While most of the metals analyzed such as As, Cd, Cu, Fe, and Pb in the leachates showed increasing leachability with an increase in fly ash content in the concrete, Ni showed a slight decreasing trend. In fact, most of the Ni was probably from the portland cement. Nickel, therefore, showed decreasing trend with increasing fly ash content because the cement content in concrete with higher fly ash content was lower. No significant trend was observed for Cr with an increase in the fly ash content. Zinc in the leachates appeared to increase somewhat with an increase on the fly ash content, and the significantly higher value for the concrete with 10% fly ash (T10) is probably due to experimental error.

Effect of w/cm--Figure 4 shows the effect of the w/cm of concrete on the concentrations of As, Cu, Ni, and Zn in the leachates from the concrete in the TCLP leaching test. From the results shown in Table 11 and Figure 4, it appears that w/cm

of concrete did not have any significant effect on the leachability of Cd, Cr, Ni, and Pb. However, as the fly ash content in the concrete with a high w/cm is lower than that with a low w/cm, the leachability of Cd and Cr actually increased with increasing w/cm due to the increased porosity of the concrete. Copper, Fe, and Zn showed increasing concentrations with increasing w/cm even though the fly ash content was lower for the concrete with a higher w/cm. Arsenic showed a decreasing trend with an increase in the w/cm. By calculating leached As per kg of the fly ash in the concrete, it seems that the w/cm did not have significant effect on the leaching, and the fly ash content appeared to be a controlling factor on the leaching of As.

Effect of curing--As shown in Table 12, the length of the moist curing does not seem to have significant effect on the leaching of the above metal elements.

CONCLUSIONS

Fly Ash

The concentrations of all regulated elements Ag, As, B, Ba, Cd, Cr, Cu, Hg, Pb, and Se in the leachates from the nine fly ashes tested were within the limits of the United States Environment Protection Agency and the Transportation of Dangerous Goods Act Regulations of Canada. The concentrations of Ag, B, Ba, Cd, Cu, Hg, and Pb were all at least an order of magnitude below the above limits. The leaching of As, B, Ni, and Se from the fly ashes appeared to increase with an increase in their content in the fly ashes; however, there were some exceptions. In general, the concentration of As leached from the fly ashes derived from the bituminous coals was much higher than that from the lignite or sub-bituminous coals.

Fly Ash Concrete

Regardless of the type and percentage of the fly ash used, w/cm of the concrete, and curing condition, none of the trace metals in the leachates from the fly ash concrete samples exceeded the regulated concentration limits by the United States Environment Protection Agency and the Transportation of Dangerous Goods Act regulations of Canada. The concrete incorporating the fly ashes is, therefore, considered stable.

In general, all the fly ash concrete samples showed similar or higher values of the metals (As, Cd, Cu, Fe, Ni, Pb, Se, Zn) when compared with the control portland cement concrete except for Cr. Chromium values for the fly ash concrete samples tested were similar to or lower than those of the control portland cement concrete.

Arsenic showed a correlation between the metal content in fly ash and the concentration of the metal leached from the fly ash concrete. The total concentration of arsenic leached from the concrete with a w/cm of 0.50 and incorporating 60% Ligan fly ash, that contained the greatest concentration of arsenic of the fly ash concrete tested, was less than 0.5% of the total available arsenic from the fly ash in the concrete. Other metals analyzed did not show such a relationship.

Most of the metals analyzed such as As, Cd, Cu, Fe, and Pb in the leachates showed increasing leachability with an increase in the fly ash content in the concrete.

Cadmium, Cr, Cu, Fe, and Zn in the leachates showed increased concentrations with increasing w/cm even though the fly ash content was lower for concrete with a higher w/cm. The leaching of As did not seem to be affected significantly by the w/cm of the concrete.

The length of moisture curing period did not have significant effect on the leaching of the trace metals from the fly ash concrete.

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Table 1 - Physical properties and chemical composition of the fly ashes used

	Fly ash								
	Point Tupper	Lingan	Sundance	Genesee	Forestburg	Thunder Bay	Belledune	Belews Creek	Coal Creek
Coal type	bituminous		sub-bituminous			lignite	Bituminous B (Columbia) + Bituminous A (Minto, NB)	bituminous	lignite
Specific gravity	2.58	2.82	2.08	1.95	1.97	2.43	2.56	2.28	2.44
Fineness									
-passing 45µm, %	75.2	87.4	83.6	63.5	78.6	89.7	85.6	79.8	76.1
-specific surface, Blaine, cm ² /g	2270	2730	3060	1960	2230	2400	2076	2270	2050
-median particle size (µm)	14	14	12.4	21.2	17.8	13.2	-	-	-
Water requirement, %	95.6	97.9	99.2	95.9	93.5	93.0	97.1	94.7	94.7
Pozzolan Activity Index, %									
-7-day	79.6	84.1	94.5	81.7	82.4	85.1	86.4	77.5	85.7
-28-day	89.2	88.6	106.9	84.5	91.0	104.3	87.7	86.8	88.9
Silicon dioxide (SiO ₂)	42.74	36.85	52.35	62.56	56.75	41.99	53.94	56.2	50.5
Aluminum oxide (Al ₂ O ₃)	20.29	18.35	23.35	20.85	21.51	21.44	16.61	30.0	15.4
Ferric oxide (Fe ₂ O ₃)	23.71	35.05	4.65	4.45	4.89	4.45	20.53	5.1	8.8
Calcium oxide (CaO)	4.17	3.68	13.38	5.83	8.83	15.81	0.31	1.1	15.6
Magnesium oxide (MgO)	1.22	1.04	1.28	1.45	1.58	3.18	1.14	0.8	4.0
Sodium oxide (Na ₂ O)	0.88	0.77	3.60	2.51	3.89	7.03	0.42	0.3	2.5
Potassium oxide (K ₂ O)	2.56	1.64	0.58	1.72	1.14	0.36	1.94	2.2	2.0
Equivalent alkali (Na ₂ O+0.658K ₂ O)	2.56	1.85	3.98	3.64	4.64	7.27	1.70	1.8	3.8
Phosphorous oxide (P ₂ O ₅)	0.68	0.26	0.20	0.12	0.36	0.58	0.78	0.2	0.1
Titanium oxide (TiO ₂)	0.86	0.87	0.75	0.67	0.51	1.05	0.78	1.7	0.7
Sulphur trioxide (SO ₃)	1.60	1.76	0.21	0.08	0.08	1.79	0.65	0.4	1.5
Loss on ignition	2.44	2.36	0.32	0.26	0.27	0.75	3.34	2.1	0.3
Carbon (C)	-	-	-	-	-	-	2.97	-	-

Table 2 - Trace element content of the fly ashes used

Element	Trace element content (g/t)									Content in coal ash [8], g/t	Content in cement [9], g/t	Content in soil [8], g/t
	Point Tupper	Lingan	Sundance	Genesee	Forestburg	Thunder Bay	Belledune	Belews Creek	Coal Creek			
Ag	<0.5	0.5	<0.5	<0.5	<0.5	<0.5	0.5	0.5	<0.5	0.04-36	6.75-19.9	-
As	688	980	26	<10	47	20	505	60	110	2.3-6,300	5-71	1 - 93
B-tot	100	95	530	360	1600	1300	180	140	860	10-5,000		-
Ba	2200	680	3800	2900	4000	8200	760	830	4600	1-13,800	91-1,402	
Be	<20	<20	<20	<20	<20	<20	<20	30	<20		0.32-3.05	
Br	<20	<20	<20	<20	<20	<20	<20	<20	<20			
Cd	24	35	<5	<5	<5	<5	30	<5	<5	0.1-130	0.03-1.12	0.01 - 0.7
Cl	67	60	27	11	19	43	16	12	15	13-1,720		
Co	240	300	54	47	34	44	28	120	88			
Cr	99	81	21	60	31	24	57	150	68	3.6-900	25-422	1 - 1,000
Cu	120	130	54	57	36	65	91	200	81	14-2,200		2 - 300
F	100	200	400	200	<100	200	<100	200	300	0.4-610		
Ga	17	21	25	17	30	10	21	32	20			
Ge	41	43	7	8	9	11	21	17	10			
Hg	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.005-12	<0.001-0.039	
La	49	49	68	47	61	54	<50	90	28			
Mn	750	980	480	280	140	91	700	94	570	25-3,000		
Mo	220	200	170	160	200	170	70	260	120	1.2-236		
Ni	100	120	39	33	29	33	18	150	55	1.8-4,300	10-129	5 - 500
Pb	160	280	48	27	49	42	38	54	19	3-2,120	1-75	2 - 200
Sb	17	17	9	5	6	9	16	12	13		0.7-4.0	
Se	35	36	23	28	21	27	18	74	30	0.8-131		
Si	2.8	4.1	1.8	3.6	9.9	9.0	12	17	8.1	0.2-134	0.62-2.23	0.1 - 4
Sn	<20	<20	<20	<20	<20	<20	<20	<20	<20			
Sr	590	520	960	790	1400	3800	290	580	1700	30-7,600		
Ti	<10	<10	<10	<10	<10	<10	<10	<10	<10			
V	160	190	69	120	56	75	240	310	150	12-1,180		
Y	30	34	37	31	31	33	41	66	31			
Yb	<5	<5	<5	<5	<5	<5	<5	<5	<5			
Zn	170	290	44	57	55	22	200	100	47	14-3,500		10 - 300
Zr	141	131	381	306	349	458	157	349	258			

Table 3 - Physical properties and chemical composition of the cement

	ASTM Type I cement
<u>Physical tests</u>	
Specific gravity	3.15
Fineness	
-passing 45 μ m, %	94
-specific surface, Blaine, cm ² /g	4100
Compressive strength of 51 mm cubes, MPa	
-3-day	26.0
-7-day	31.9
Time of setting, Vicat test, min	
-initial setting	220
-final setting	325
Air content of mortar, volume %	5.5
<u>Chemical analyses, %</u>	
Silicon dioxide (SiO ₂)	20.3
Aluminium oxide (Al ₂ O ₃)	4.2
Ferric oxide (Fe ₂ O ₃)	3.0
Calcium oxide (CaO)	62.0
Magnesium oxide (MgO)	2.8
Sodium oxide (Na ₂ O)	0.3
Potassium oxide (K ₂ O)	0.9
Equivalent alkali (Na ₂ O+0.658K ₂ O)	0.9
Phosphorous oxide (P ₂ O ₅)	0.2
Titanium oxide (TiO ₂)	0.2
Sulphur trioxide (SO ₃)	3.5
Loss on ignition	2.0
<u>Bogue potential compound composition</u>	
Tricalcium silicate C ₃ S	56
Dicalcium silicate C ₂ S	16
Tricalcium aluminate C ₃ A	6
Tetracalcium aluminoferrite C ₄ AF	9

Table 4 - Grading of the Aggregates

Coarse aggregate		Fine aggregate	
Sieve size (mm)	Cumulative percentage retained	Sieve size (mm)	Cumulative percentage retained
19.0	0	4.75	0.0
12.7	30	2.36	10.0
9.5	70	1.18	32.5
4.75	100	0.60	57.5
		0.30	80.0
		0.15	94.0
		pass	100.0

Table 5 - Mixture Proportions of Concrete

Mix No	Fly ash, source	Fly ash, %	W/ (C+FA)	kg/m ³						AEA, mL/m ³
				Water	Cement	Fly ash	Sand	CA	SP	
T0	-	0	0.5	160	321	0	746	1129	0	86
T1	Point Tupper	30	0.5	160	224	96	724	1096	0	120
T2	Lingan			161	226	97	734	1109	0	130
T3	Sundance			161	225	97	718	1089	0	201
T4	Genesee			158	222	95	704	1067	0	109
T5	Forestburg			162	226	97	720	1089	0	115
T6	Thunder Bay			161	225	96	725	1098	0	71
T7	Belledune			162	226	97	733	1108	0	346
T8	Belews Creek			159	223	95	716	1082	0	228
T9	Coal Creek			161	225	97	727	1100	0	71
T10	Lingan	10	0.5	161	289	32	737	1107	0	95
T11		20		160	256	64	733	1100	0	110
T12		40		160	192	128	732	1098	0	171
T13		50		160	160	160	729	1092	0	171
T14		60		160	128	192	729	1093	0	200
T15	Lingan	30	0.4	160	280	120	701	1053	1.7	143
T16			0.6	162	189	81	761	1139	0	87
T17			0.7	158	158	68	757	1136	0	56
T18	Lingan	56	0.32	120	166	211	750	1124	7.1	344
T19	Forestburg			121	167	212	718	1081	5.1	317

CA - coarse aggregate

SP - superplasticizer, naphthalene-based

AEA - air-entraining admixture

Table 6 - Properties of Concrete

Mix No	Fly ash, source	Fly ash, %	W/ (C+FA)	Temperature, °C	Slump, mm	Unit weight, kg/m ³	Air content, %	Density at 1 day, kg/m ³	Compressive strength, MPa	
									7-day	28-day
T0	-	0	0.5	-	65	2364	5.6	2390	29.1	34.3
T1	Point Tupper	30	0.5	24.5	115	2335	6.1	2363	20.0	27.5
T2	Lingan			23.5	90	2364	5.3	2377	21.5	29.1
T3	Sundance			23	150	2321	5.5	2349	21.1	33.9
T4	Genesee			24	135	2293	6.9	2316	17.8	24.8
T5	Forestburg			23.5	165	2335	5.0	2345	18.6	28.2
T6	Thunder Bay			23.5	165	2335	5.6	2364	23.0	33.4
T7	Belledune			25	125	2349	5.1	2376	20.5	26.9
T8	Belews Creek			25	100	2293	6.6	2308	17.9	26.1
T9	Coal Creek			19.5	170	2335	5.4	2362	21.0	29.5
T10	Lingan	10	0.5	20.5	90	2349	5.6	2384	29.6	35.0
T11		20		19.5	125	2321	6.0	2327	24.5	29.8
T12		40		21	125	2335	5.8	2354	17.8	26.8
T13		50		19	140	2321	6.2	2353	12.9	21.3
T14		60		-	180	2335	5.9	2355	9.0	15.3
T15	Lingan	30	0.4	-	140	2349	6.0	2379	29.0	36.3
T16			0.6	19	95	2364	4.9	2378	15.7	22.9
T17			0.7	-	210	2307	6.9	2333	9.6	13.7
T18	Lingan	56	0.32	20.5	210	2406	5.5	2444	27.0	41.3
T19	Forestburg			19.5	230	2364	5.1	2407	30.9	48.4

Table 7 - Leachability of fly ashes

Element	Concentration measured in fly ash leachate, ppm									Concentration measured in portland cement leachate [9] ppm
	Point Tupper	Lingan	Sundance	Genesee	Forestburg	Thunder Bay	Belledune	Belews Creek	Coal Creek	
Ag	<0.007	<0.004	<0.004	<0.004	<0.004	<0.009	<0.002	<0.004	<0.004	0.003-0.12
As	0.939	0.975	0.096	0.061	0.093	<0.014	1.317	0.850	0.022	0.005-0.084
B	0.2	0.2	15.9	9.6	20.4	23.3	3.7	1.9	23.5	
Ba	0.640	0.476	1.826	1.512	1.021	0.240	0.195	0.243	0.280	0.49-4.27
Cd	<0.001	<0.001	0.007	0.004	0.022	0.012	0.028	<0.001	0.013	0.0003-0.0123
Co	<0.001	<0.001	0.067	0.018	0.016	0.033	0.018	<0.001	0.062	
Cr	0.050	0.043	0.329	0.661	0.194	0.164	0.070	0.038	0.364	0.07-1.54
Cu	<0.015	<0.015	0.088	0.040	0.057	0.081	0.449	<0.015	0.045	
F	<1	<1	13	6	2	2	1.5	<1	<1	
Fe	<0.2	<0.2	31.9	18.4	18.6	2.9	<0.1	<0.2	1.1	
Hg	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	<0.0002	0.0001-0.0050
Mn	-	-	2.104	-	-	-	1.076	-	-	
Ni	<0.013	<0.013	0.122	0.040	0.046	0.164	0.076	<0.013	0.228	0.06-0.17
Pb	0.021	0.010	0.010	0.007	0.058	0.015	<0.001	0.001	0.006	0.002-0.029
Se	0.024	0.046	0.036	0.041	0.084	0.101	0.129	0.550	0.031	0.001-0.025
Tl	0.0213	0.0101	<0.002	<0.002	0.0039	<0.002		0.0025	<0.002	0.002-0.028
U	0.001	0.001	0.131	0.069	0.041	0.031	<0.002	0.003	0.082	
V	0.113	0.170	0.179	0.232	0.090	0.052	0.171	1.245	0.045	
Zn	<0.1	<0.1	0.3	0.2	0.4	0.2	0.3	<0.1	0.2	
Zr	<0.1	<0.1	0.2	0.1	<0.1	<0.1	<0.2	<0.1	<0.1	

Table 8: Leachate Quality Criteria (concentrations in ppm)

Inorganic Parameter	Leachate Extraction Procedure					
	EPA, U.S.A. EP Tox	EPA, U.S.A. TCLP	Ontario LEP*	Quebec	B.C. SWEP	TDGR** (CGSB LEP)
Silver (Ag)	5.0	5.0	-	-	-	-
Arsenic (As)	5.0	5.0	5.0	5.0	5.0	5.0
Boron (B)	-	-	-	500	-	500.0
Barium (Ba)	100	100	-	100	-	100.0
Cadmium (Cd)	1.0	1.0	0.5	0.5	0.5	0.5
Chromium (Cr)	5.0	5.0	5.0	5.0	5.0	5.0
Copper (Cu)	-	-	-	-	100.0	100.0
Mercury (Hg)	0.2	0.2	-	0.1	-	0.1
Manganese (Mn)	-	-	-	-	-	5.0
Lead (Pb)	5.0	5.0	5.0	5.0	5.0	5.0
Selenium (Se)	1.0	1.0	1.0	1.0	1.0	-
Zinc (Zn)	-	-	-	-	500.0	-
Total Metals	-	-	-	10	-	-

* Obtained by multiplying the quality criteria of the Ontario Leachate Extraction Procedure (OLEP) by 100 to obtain the concentration limit in the waste extract

TDGR - Transportation of Dangerous Goods Regulations. The TDGR incorporated the Leachate Extraction Procedure CGSB 164-GP-1MP.

Table 9 - TCLP test results, Effect of the source of fly ash (concrete was cured for 7 days in moisture condition and 21 days in laboratory air)

Mix No	Fly ash source	Fly ash, %	W/(C+FA)	Concentration measured in leachate, ppm									pH
				As	Cd	Cr	Cu	Fe	Ni	Pb	Se	Zn	
T0†	-	0	0.5	<0.002	<0.001	0.042	0.014	<0.02	0.161	<0.001	<0.023	0.28	6.4
T1	Point Tupper	30	0.5	0.009	0.001	0.023	0.035	0.12	0.150	0.002	<0.023	0.44	6.0
T2	Lingan			0.010	0.002	0.024	0.030	0.14	0.143	0.005	<0.023	0.41	6.0
T3	Sundance			<0.002	<0.001	0.026	0.058	0.27	0.141	0.002	<0.023	0.50	5.6
T4	Genesee			<0.002	<0.002	0.025	0.037	0.10	0.012	0.002	<0.042	0.66	5.8
T5	Forestburg			<0.001	<0.004	0.025	0.027	<0.10	0.145	<0.013	<0.016	0.41	5.9
T6	Thunder Bay			<0.001	<0.004	0.027	0.029	<0.10	0.140	<0.013	<0.016	0.34	5.9
T7	Belledune			0.008	<0.002	0.023	0.032	<0.10	0.182	<0.001	<0.042	0.47	5.9
T8	Belews Creek			<0.002	<0.002	0.024	0.034	<0.10	0.204	<0.001	<0.042	0.42	5.9
T9†	Coal Creek			0.001	0.002	<0.031	0.045	0.39	0.142	<0.003	<0.007	0.32	6.0
T18†	Lingan	56	0.32	0.018	0.004	0.035	0.106	1.03	0.117	0.009	<0.007	0.50	5.4
T19	Forestburg			<0.001	0.002	0.039	0.095	1.43	0.108	0.003	<0.007	0.44	5.3

† Average of the results of two analyses

Table 10 - TCLP test results, Effect of fly ash content (concrete was cured for 7 days in moisture condition and 21 days in laboratory air)

Mix No	Fly ash, source	Fly ash, %	W/(C+FA)	Concentration measured in leachate, ppm									pH
				As	Cd	Cr	Cu	Fe	Ni	Pb	Se	Zn	
T0†	-	0	0.5	<0.002	<0.001	0.042	0.014	<0.02	0.161	<0.001	<0.023	0.28	6.4
T10	Lingan	10		0.006	<0.002	0.023	0.017	<0.10	0.176	<0.001	<0.042	1.28	6.2
T11†		20		0.010	<0.002	0.022	0.021	<0.10	0.175	<0.001	<0.042	0.35	6.3
T2		30		0.010	0.002	0.024	0.030	0.14	0.143	0.005	<0.023	0.41	6.0
T12		40		0.016	0.002	0.023	0.044	0.17	0.184	0.008	<0.042	0.45	5.8
T13		50		0.014	0.004	<0.031	0.110	0.53	0.127	0.005	<0.007	0.49	5.5
T14		60		0.017	0.006	0.040	0.158	1.73	0.113	0.010	<0.007	0.58	5.3

† Average of the results of two analyses

Table 11 - TCLP test results, Effect of w/cm (concrete was cured for 7 days in moisture condition and 21 days in laboratory air)

Mix No	Fly ash, source	Fly ash, %	Fly ash content, kg/m ³	W/(C+FA)	Concentration measured in leachate, ppm									pH
					As	Cd	Cr	Cu	Fe	Ni	Pb	Se	Zn	
T0†	-	0	0	0.5	<0.002	<0.001	0.042	0.014	<0.02	0.161	<0.001	<0.023	0.28	6.4
T15	Lingan	30	120	0.4	0.020	0.002	0.037	0.016	<0.20	0.143	<0.003	<0.007	0.20	6.4
T2			97	0.5	0.010	0.002	0.024	0.030	0.14	0.143	0.005	<0.023	0.41	6
T16			81	0.6	0.007	0.002	<0.031	0.083	0.45	0.134	0.003	<0.007	0.49	5.6
T17			68	0.7	0.007	0.003	<0.031	0.061	0.57	0.187	<0.003	<0.007	0.59	5.9
T14	Lingan	60	192	0.5	0.017	0.006	0.040	0.158	1.73	0.113	0.010	<0.007	0.58	5.3
T18†		56	211	0.32	0.018	0.004	0.035	0.106	1.03	0.117	0.009	<0.007	0.50	5.4

† Average of the results of two analyses

Table 12 - TCLP test results, Effect of curing

Mix No	Fly ash, source	Fly ash, %	W/(C+FA)	Curing, days		Concentration measured in leachate, ppm									pH
				moist	lab air	As	Cd	Cr	Cu	Fe	Ni	Pb	Se	Zn	
T0	-	0	0.5	1	27	<0.002	<0.001	0.035	0.01	<0.02	0.158	0.002	<0.023	0.23	6.5
				7	21	<0.002	<0.001	0.042	0.01	<0.02	0.161	0.001	<0.023	0.28	6.4
				28	0	<0.002	<0.001	0.045	0.01	<0.02	0.158	0.002	<0.023	0.26	6.4
T2	Lingan	30	0.5	1	27	0.013	0.002	0.026	0.03	0.09	0.155	0.005	<0.023	0.44	6.0
				7	21	0.010	0.002	0.024	0.03	0.14	0.143	0.005	<0.023	0.41	6.0
				28	0	0.010	0.002	0.022	0.03	0.10	0.199	<0.001	<0.023	0.40	6.0
T5	Forestburg	30	0.5	1	27	<0.001	<0.004	0.021	0.03	<0.10	0.145	<0.013	<0.016	0.30	5.9
				7	21	<0.001	<0.004	0.025	0.03	<0.10	0.145	<0.013	<0.016	0.41	5.9
				28	0	<0.001	<0.004	0.025	0.04	0.43	0.135	<0.013	<0.016	0.34	5.7
T14	Lingan	60	0.5	1	27	0.013	0.009	0.034	0.18	1.66	0.121	0.008	<0.007	0.57	5.4
				7	21	0.017	0.006	0.040	0.16	1.73	0.113	0.010	<0.007	0.58	5.3
T15	Lingan	30	0.4	1	27	0.024	0.003	<0.031	0.04	<0.20	0.141	<0.003	<0.007	0.43	6.2
				7	21	0.020	0.002	0.037	0.02	<0.20	0.143	<0.003	<0.007	0.20	6.4
T17	Lingan	30	0.7	1	27	0.010	0.003	<0.031	0.09	0.89	0.129	<0.003	<0.007	0.56	5.7
				7	21	0.010	0.003	<0.031	0.06	0.57	0.187	<0.003	<0.007	0.59	5.9

The results of the concrete sample T0 cured for 7 days in moist room and 21 days in laboratory air are the average of two analyses

Table 13 - Summary of Leaching Trends Observed from TCLP Test

Metal Concentrations in leachate from concrete increase with increasing:	Observed Trend							
	As	Cd	Cr	Cu	Ni	Pb	Se	Zn
Content of Metal in Fly Ash	yes	no	no	no	no	no	-	no
Leachability of Fly Ash	yes	-	no	no	no	-	-	no
% Fly Ash in Concrete	yes	~yes	no	yes	no	~yes	-	~yes
Water/Binder Ratio	no	yes	~yes	yes	no	no	-	yes

yes = trend increase/decrease

no = no trend observed

- = can't interpret due to detection limits

Table 14: Percentage of Total Arsenic Leached from the concrete incorporating 60% Lingnan fly ash (Mixture T14)

Test Method	Duration of test	Mass of Concrete (g)	Leachant Volume (L)	Liquid/solid ratio	Available Arsenic (mg)	[As] in Leachant (ppm)	Total As Leached (mg)	% Arsenic Leached
TCLP	18 hrs	100	2	20:1	8	0.017	0.034	0.43

* In this test, no analyses were performed at the end of the first five weeks. The only analyses were performed at the end of the sixth weeks. It was assumed that at the end of each week, the metal content leached was the same as that leached in week six.

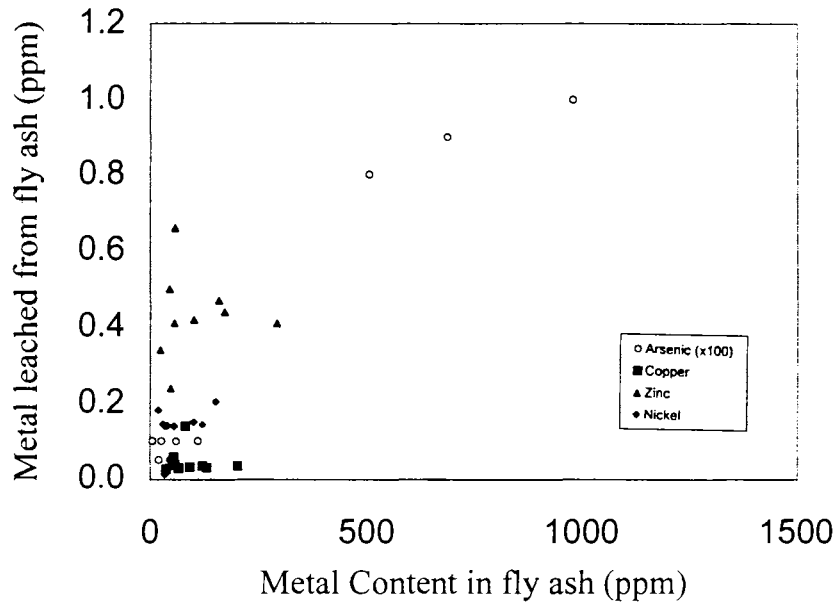


Fig. 1 - Comparison of the trace metal contents of the fly ashes and the metals leached from fly ashes in TCLP leaching test.

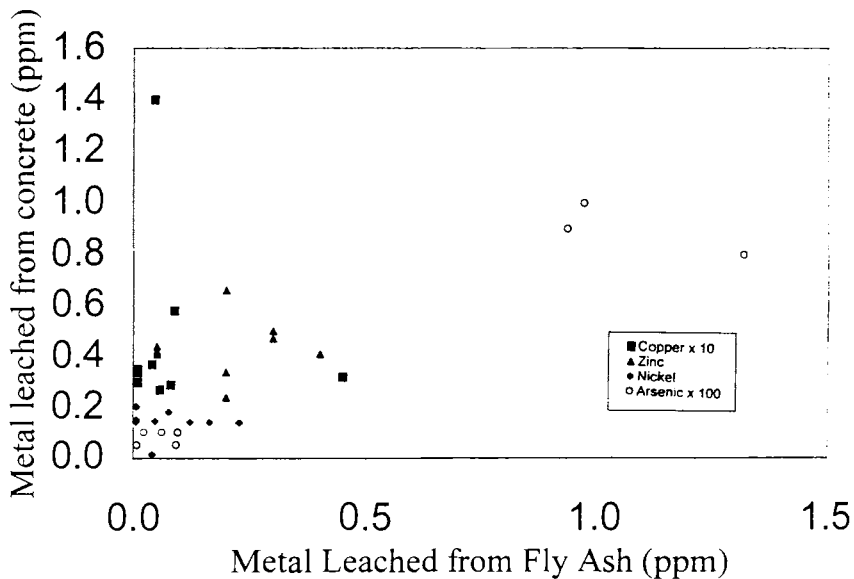


Fig. 2 - Comparison of the trace metals leached from the fly ashes and those leached from the concrete incorporating the fly ashes using TCLP test.

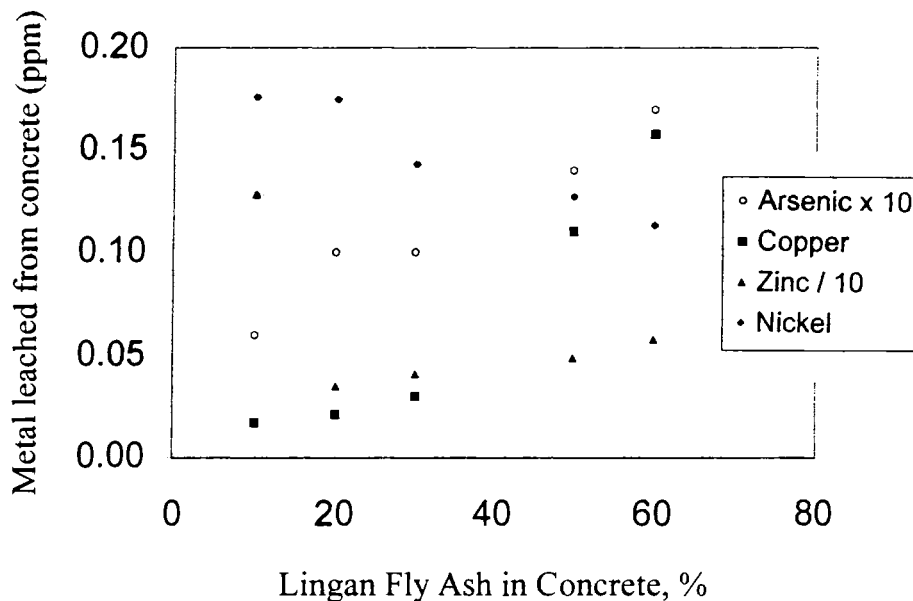


Fig. 3 - Effect of the fly ash content in concrete incorporating Lingam fly ash on the concentrations of As, Cu, Ni, and Zn in the leachates from concrete in the TCLP leaching test.

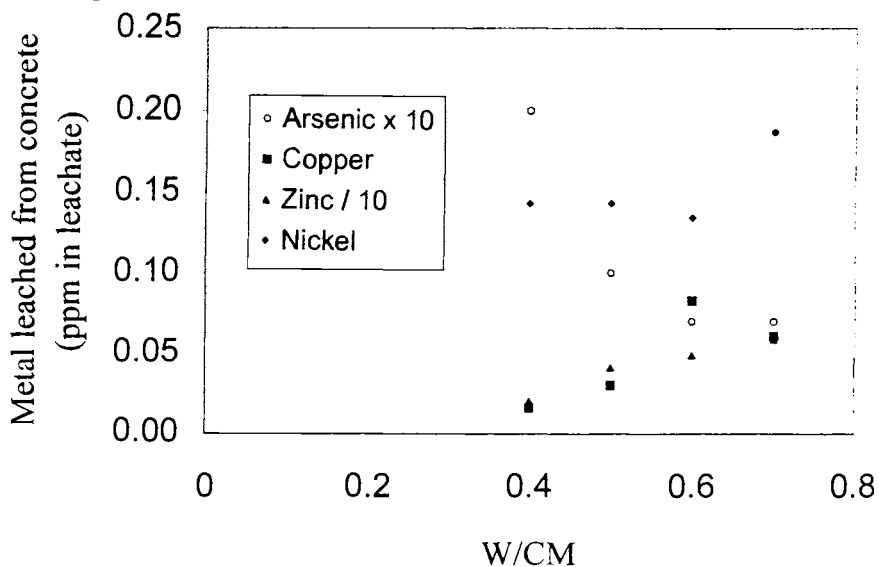


Fig. 4 - Effect of the w/cm of concrete on the concentrations of As, Cu, Ni, and Zn in the leachates from concrete in TCLP leaching test.

Classification of Fly Ash According to Japan Industrial Standard, JIS A 6201-1999

**by S. Nagataki, F. Tomosawa, T. Kanazu,
and T. Yamamoto**

The Japan Industrial Standard (JIS) of “Fly Ash for Use in Concrete, JIS A 6201,” was revised in 1999 in order to widen the utilizable amount of fly ash as a mineral admixture. The featured points in this revision were that; [1] fly ash with high loss on ignition (LOI) ranging from 5.0% to 8.0% is specified as Class-III, [2] fly ash with low Blaine fineness ranging from 1500cm²/g to 2500cm²/g is specified as Class-IV, [3] high quality fly ash with LOI less than 3.0% and Blaine fineness more than 5000cm²/g was specified as Class-I. Most of the fly ash qualified in JIS A 6201-1996 would be specified as Class-II. Class-III and Class-IV fly ash wouldn’t meet the requirement of JIS A 6201-1996. This paper describes the background and the contents of the revision of JIS A 6201.

Keywords: fly ash; Japan industrial standard; mineral admixture; utilization

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INTRODUCTION

Total amount of fly ash exhausted from pulverized-coal burning power plants was about six million tons in 1998 in Japan. Those generating capacity will increase largely in the near future because of safety and stable supply and economical merit of imported fuel coals. Therefore the amount of exhausted coal ash will be 1.5 times larger than the current amount, and this condition will bring shortage of disposal sites. Moreover, the revision of the law for disposal method of waste materials will restrict the landfill disposal. These situations will bring a need for enlarging the utilization amount of fly ash in cement concrete usage, i.e., mineral admixture that is thought to be the most effective way to utilize coal ash. JIS A 6201, the code of fly ash for use in concrete, was revised in February 1999 to accelerate the usage as a mineral admixture. This paper describes the background and the content of JIS A 6201-1999.

QUALITY OF FLY ASH IN JAPAN

Quality of fly ash in Japan had changed widely in 1970's because of the following factors;

- [1] More than 80% of fuel coal for generating electricity is imported in Japan. Most of the imported coal has a high melting point as compared with that of domestic coal. The change in the property of fuel coal may be a factor that would increase the rate of non-spherical shape of fly ash.
- [2] The combustion temperature in the boiler is generally controlled under about 1300°C to reduce the amount of nitrogen oxide in exhausted gas. Lower temperature in the boiler relatively to the melting point of fuel-coal increases a rate of non-spherical shape of fly ash.
- [3] There is a need to change the burning condition of the boiler at the power

plant according to local change in the demand of electricity. The change in the burning condition brings a change in the characteristics of fly ash.

- [4] Fuel coals are imported from more than forty places of production in foreign countries. The variety in types of coals leads to a change in characteristics of the fly ash.

Figure 1 shows the domestic data of loss on ignition (LOI) of fly ash investigated in 1995, the exhausted amount of which was about 3.4 million tons. As shown in Fig.1, more than 80 % of total ash showed LOI less than 5.0 % and about 95 % of the ash showed LOI less than 8.0 %. With the exception of part of samples, the quality of fly ash based on the LOI is good.

CHANGES OF JIS A 6201 – FLY ASH FOR USE IN CONCRETE

More than forty years had passed since the first establishment of JIS of fly ash for use in concrete and more than twenty years had passed since the last revision of JIS A 6201 in 1974, and then the work in revising the JIS A 6201 had begun in 1994 (Table-1). During the long term, the changes in the quality of fly ash had been brought about as mentioned above. In the revision that was established in 1999, not only the specified values but also the specified items were considered. The outline of the changes in JIS of fly ash for use in concrete, from the earliest standard to the latest, are the followings;

(1) Standardization in Large Dam Committee (original form of JIS A 6201)

The standard was established in September 1956. Though the specified items were almost the same as JIS A 6201-1999, the water demand ratio was used to estimate the flowability of fly ash mortar. The value was defined as a ratio of the amount of mixing water (W_r) to obtain 200±5 mm in flow value of the control mortar to that of the test mortar (W_t), i.e. $W_t/W_r \times 100$ (%). The replacement ratio of fly ash to cement was 30 %. Mortar specimens used for estimating its pozzolanic reactivity were cured in the water at the temperature of 40±1°C for 7 days and 28 days.

(2) Establishment of JIS A 6201-1958

JIS of fly ash for use in mortar and concrete as an admixture was established in 1958. There was much difference from the standard of Large Dam Committee, excepting the moisture content and LOI. The unit water ratio similar to the water demand ratio was specified for estimating the flow-ability of the test mortar. The replacement ratio of fly ash was 25% and water cement ratio of both the test and the reference mortars was 65 %. Test specimens for evaluating

strength development were cured in $20\pm 1^{\circ}\text{C}$ water for 28 days and 91 days.

(3) First revision of JIS A 6201 in 1974

Main fuel in the steam power plants changed from coal to heavy oil around 1970, however the demand for fly ash still increased. A shortage of fly ash brought a need to extend the limit of the specified values in JIS A 6201 without having any influence in the usage. The limit for Blaine fineness was lowered from $2700\text{cm}^2/\text{g}$ to $2400\text{cm}^2/\text{g}$ with extending the limit value on the unit water ratio and the compressive strength ratio, and the $45\mu\text{m}$ sieve test was eliminated from the fineness estimation. Especially the unit water ratio determined from the flow test had a good relation with the strength development, i.e. higher the unit water ratio, the lower the compressive strength.

MAIN POINTS IN REVISING JIS A 6201 IN 1996 AND 1999

There are three important points in promoting the utilization of fly ash; (1) controlling the change of the quality of fly ashes, (2) stability in supplying, (3) lowering the price. Many users of fly ash suggested these three points in a market survey. The principal objective in revising JIS A 6201 was to make familiar conditions in the standard for the users of fly ash, i.e. the revision of the specified values and the test methods.

The revision work started in 1994 and continued till 1999. In these six years JIS A 6201 was revised twice. The main points are shown below.

SECOND REVISION IN JIS A 6201 IN 1996

Revised contents are the followings.

- [1] Flow value ratio was specified instead of unit water ratio.
- [2] Pozzolanic activity index (AI) was specified instead of compressive strength ratio.
- [3] $45\mu\text{m}$ sieve test and its limit value were introduced again.

Flow value ratio

Much skill is needed in performing in the flowability test to obtain unit water ratio according to JIS A 6201-1974. There was a problem to bring rather large difference among the data even in using the same fly ash. Flow value ratio was introduced to avoid this problem. Mix proportion of test mortar was fixed and the flow value ratio was obtained by dividing a flow value of fly ash mortar by that of a control mortar. The mix proportion of the mortar and the mixing method followed the EN 450 (cement/sand : 1/3, water/(cement + fly ash) : 0.5,



fly ash replacement : 25 %)(1)(2).

Figure 2 shows the relation between unit water ratio and flow value ratio that was obtained from the test data. Both ratios were calculated in accordance with JIS A 6201-1974 and JIS A 6201-1996, respectively. There was a good linear relationship, so that the obtained data according to JIS A 6201-1974 could be translated into that specified in JIS A 6201-1996, i.e. the limit value of 102 % in unit water ratio to that of 92 % in flow value ratio.

Pozzolanic Activity Index

The mix proportion of the mortar and the mixing method for estimating pozzolanic activity of fly ash in mortar were the same as those in the case of the flow value ratio evaluation. The curing condition and the evaluation method in the mortar bar tests followed the EN 450 standard. In the last code, JIS A 6201-1974, changes in mixing water content had a large influence on the compressive strength ratio, especially on the strength development of fly ash mortar, while AI resulted mainly from pozzolanic activity of each fly ash because of its constant amount of mixing water.

Fineness of Fly Ash

The 45 μ m sieve method was adopted again in referring to the standard codes in other countries. Not only the 45 μ m sieve residue and the Blaine fineness but also the estimation that was obtained from the laser diffraction and scattering method (LD&S) were thought to be useful in estimating the fineness of fly ash. Figure 3 shows the relation between the 45 μ m sieve residue (%) and median particle size (d₅₀, μ m) obtained from LD&S method. There is a good linear relationship and this result means that the 45 μ m sieve residue is a proper index in estimating the fineness of fly ash. Also, Fig.3 shows that the LD&S method will be mainly applied in estimating the fineness of fly ash in the future.

THIRD REVISION IN JIS A 6201 IN 1999

In the revision in 1999 the followings had been performed in addition to the revised contents in 1996.

- [1] Classification of quality of fly ash into four grades
- [2] Adoption of direct measurement of carbon content
- [3] Revision of heating temperature in the LOI test method

Classification of quality of fly ash into four grades

The purpose of these revisions was to increase the utilization of fly ash in cement concrete as a concrete admixture. The important characteristics of fly ash, which would have much influence on the properties of fresh and hardened fly ash concrete, might be the fineness and LOI. As shown in Table-1, these two

characteristics were reflected in the flow value ratio and the AI. Four characteristics of fly ash, i.e. fineness, LOI, flow value ratio, and activity index, were applied in the classification of fly ash.

(1) Class-I

High quality fly ash with high fineness and low LOI could be produced by using the high performance air stream classifier or by directly gathering fine fly ash from the down stream section of the electric precipitator (EP). Figure 4 and Figure 5 shows the influences of Blaine fineness and LOI on the flow value ratio. Twenty-four fly ash samples shown in these figures were collected at each section of EP, i.e. upstream section (EP-1), middle section (EP-2) and downstream section (EP-3), of eight power stations in Japan. The flow value ratio of mortar should be affected by the fineness and LOI of fly ash, the higher the Blaine value and the lower the LOI, the higher the flow value ratio. The limits of the Blaine value and LOI for Class-I to obtain high flowability of the test mortar, i.e. 105 % in flow value ratio, were specified to be more than 5000 cm^2/g and less than 3.0 %, respectively.

(2) Class-II

Class-II fly ash basically corresponded to the fly ash specified in JIS A 6201-1996 except the limits on Blaine fineness and flow value ratio were slightly changed, i.e. more than 2500 cm^2/g in Blaine fineness and more than 95 % in flow value ratio.

(3) Class-III

The mean LOI value may be dependent mainly on the characters of each boiler, i.e. the shape and the way of combustion of the boiler, and then secondarily on the type of fuel coal. Therefore, the boilers that exhaust relatively high LOI-fly ash might be able to be determined in Japan. The establishment of Class-III would help to enhance the utilization of fly ash produced from these boilers. As shown in Fig.1, up to 15 % of fly ash would be categorized in Class-III, while about 80 % of fly ash in Class-II. The differences in the standard-limitation as compared with Class-II were that, LOI was ranging from 5.0 % to 8.0 % and the flow value ratio was more than 85 %. Figure 6 showed the relation among LOI, the flow value ratio, and AI. LOI had an influence on reducing the flow value ratio, while it hardly influenced the AI.

(4) Class-IV

Coarse fly ash, mainly derived from classified residue of the air stream classifier at power stations, was categorized as Class-IV. The other classified fly ash in this process should belong to Class-I or Class-II. Class-IV fly ash included a high percent of non-spherical particles. The flowability and strength development of the mortar that contained Class-IV fly ash may be worse than that of another class fly ash. However, the utilization for grouting material

micro-particle supplement usage to sand might be useful. The limitations of Class-IV standard were less than 5.0 % in LOI, more than 1500cm²/g in Blaine fineness, more than 75 % in flow value ratio and more than 60 % and 70 % in AI at 28 days and 91 days, respectively. As shown in Figure 7, Class-IV was categorized as the lowest quality for mineral admixture.

(5) 45 μ m sieve residue

The standard limits derived from the 45 μ m sieve residue method were decided based on the relation between 45 μ m sieve residue and the Blaine fineness. Those values should be consistent because the both of indices stand for the fineness of fly ash. The relation between two indices is shown in Figure 8. The indices of 10 %, 40%, and 70% in the 45 μ m sieve residue corresponded to 5000 cm²/g (Class-I and Class-II), 2500 cm²/g (Class-III), and 1500 cm²/g (Class-IV) in the Blaine fineness, respectively.

(6) Carbon content

Carbon content in fly ash was basically important from a view of mineral admixture usage, but LOI had been generally specified in JIS A 6201. LOI could stand for the carbon content appropriately. In this revision both methods could be applied in considering the correspondence to EN 450. Sixty data obtained in the working group showed a tendency that the carbon contents were slightly lower than LOI, i.e. 0.2 %.

(7) Loss on ignition

The heating temperature in the LOI test was raised from 750 $\pm$ 50°C to 975 $\pm$ 25°C to match with the method in EN 450. Sixty-nine data gathered through the working group and the investigated results showed that there was little difference in LOI obtained from those two different temperatures.

CONCLUDING REMARKS

The outline of JIS A 6201-1999, which was revised in February 1999, has been described. What had been done through the revision was to obtain the data on fly ashes, whose standardized items had distributed values in a wide range, and to classify the quality into four grades based on the data investigation. There is a need to continue to monitor the revised standards with field performance of the various fly ash classes. The completion of this technical issue will bring about a wider utilization of fly ash in cement concrete. As described in the introduction, the establishment of supplying system is another important issue, and then the economical cost of fly ash would be lowered. The issues concerning the cost and the quality change of fly ash should be urgently solved.

It is expected that the revision of JIS A 6201 would be the beginning of solving the disposal problem of fly ash in Japan.

ACKNOWLEDGEMENT

The authors wish to thank the committee members, who made suggestions and discussion through the revision working of JIS A 6201 from 1994 to 1999, for their great assistance.

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2. British Standard, " Method of Testing Cement Part 1. Determination of Strength", BS EN 196-1, 1995

Table 1. Changes of codes for fly ash in concrete, JIS A 6201

Items	JCOLD* ¹ 1956	JIS -1958	JIS -1974	JIS -1996	JIS-1999			
					Class- I	Class- II	Class-III	Class-IV
LOI (%) (upper limit)	5	5	5	5.0	3.0* ²	5.0* ²	8.0* ²	5.0* ²
45 μ m sieve residue (%) (upper limit)	5* ⁴	25* ⁵	-----	40* ⁶	10* ⁶	40* ⁶	40* ⁶	70* ⁶
Fineness* ³	3000	2700	2400	2400	5000	2500	2500	1500
Specific surface area (cm ² /g, blaine fineness, lower limit)								
Unit water ratio (%) (upper limit)	105* ⁷	100	102	92	105	95	85	75
Flow ratio (%) (lower limit)								
Compressive strength ratio								
7 days (%)* ⁸	55							
28 days (%)* ⁸	90							
28 days (%)		63	60					
91 days (%)		80	70					
Pozzolanic activity Index								
28 days (%)				80	90	80	80	60
91 days (%)				90	100	90	90	70
Density (g/cm ³ lower limit)	2.0	1.95	1.95	1.95	1.95			
SiO ₂ (%) (lower limit)	40	45	45	45.0	45.0			
Moisture content (%) (upper limit)	1	1	1	1.0	1.0			
Uniformity Blaine ; changing range for samples* ⁹	$\pm 15\%$	± 450	± 450	± 450	± 450			
fineness (cm ² /g, lower limit)				± 5	± 5			
Sieve residue (%) (lower limit)	± 5	± 5	± 5					
Unit water ratio (%) (lower limit)* ⁷								

*1 ; Standardization of Japan Commission on Large Dams

*2 ; Carbon content can be substituted for the analyzing LOI.

*3 ; Either one of the items, Blaine method or sieve residue method, is available for estimation.

*4 ; In case of Blaine method wasn't available, 88 μ m sieve residue was substituted.

*5 ; The estimation was in 44 μ m sieve residue.

*6 ; The Blaine value should be noted aside in case of applying sieve residue data mainly.

*7 ; Water demand ratio : $F/(C+F)=30\%$, adjusting amount of water so that the flow would be 200 ± 5 mm

*8 ; curing in $40 \pm 1^\circ\text{C}$ water after de-molding

*9 ; averaging ten continuous samples in JCOLD, warranty sample settled among user and supplier in JIS

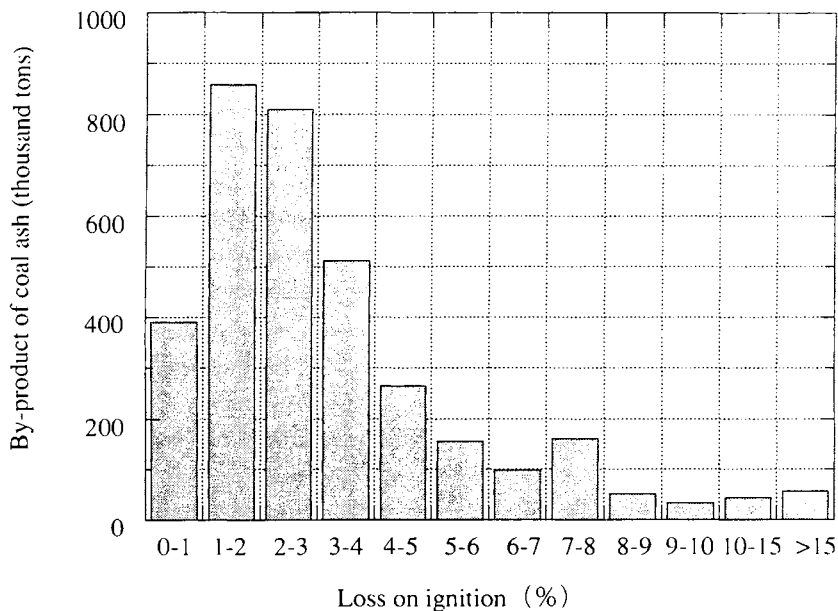


Fig.1 Relation between LOI and by-product of coal ash¹⁾

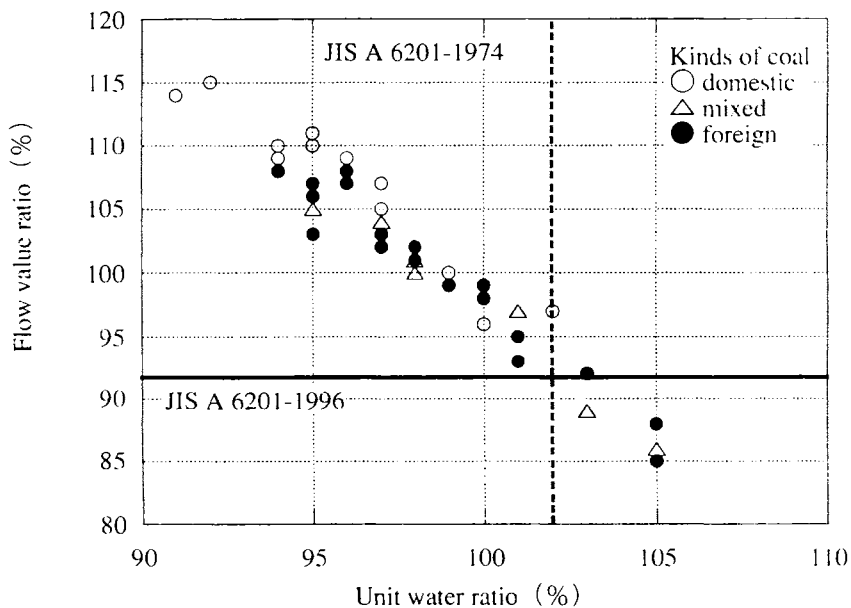


Fig.2 Relation between unit water ratio and flow value ratio

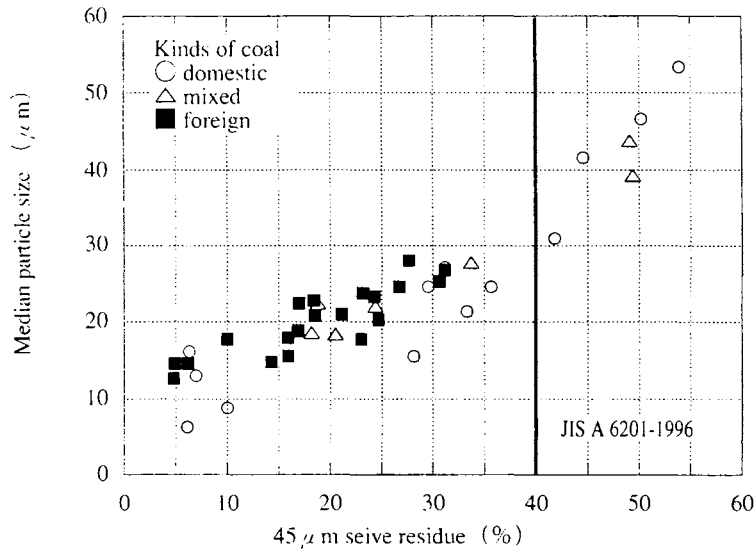


Fig.3 Relation between 45 μm sieve residue and median particle size by LD&S method

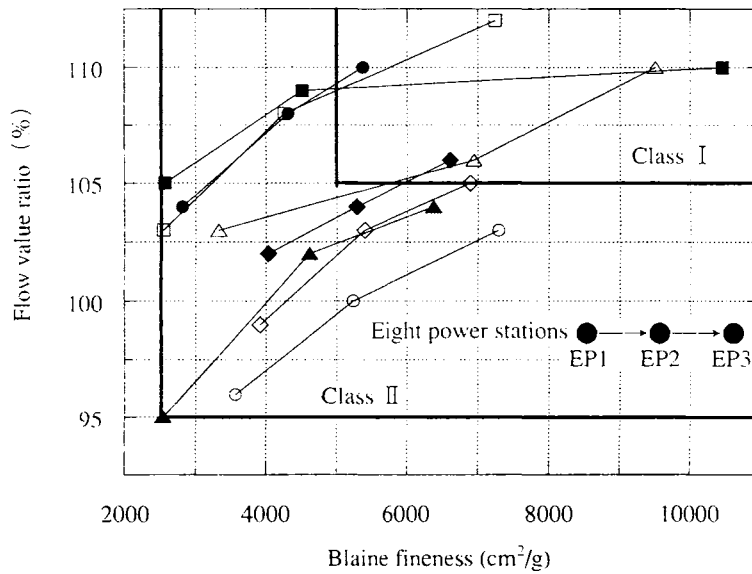


Fig.4 Relation between blaine fineness and flow value ratio

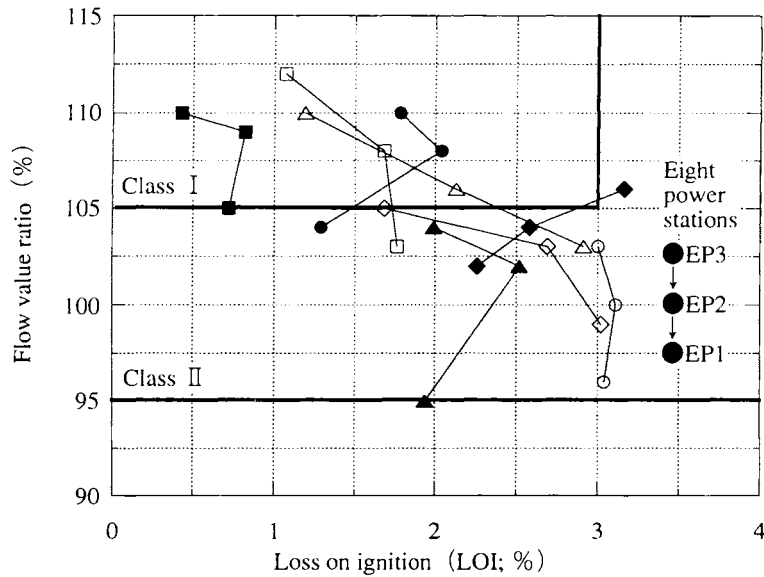


Fig.5 Relation between loss on ignition (LOI) and flow value ratio

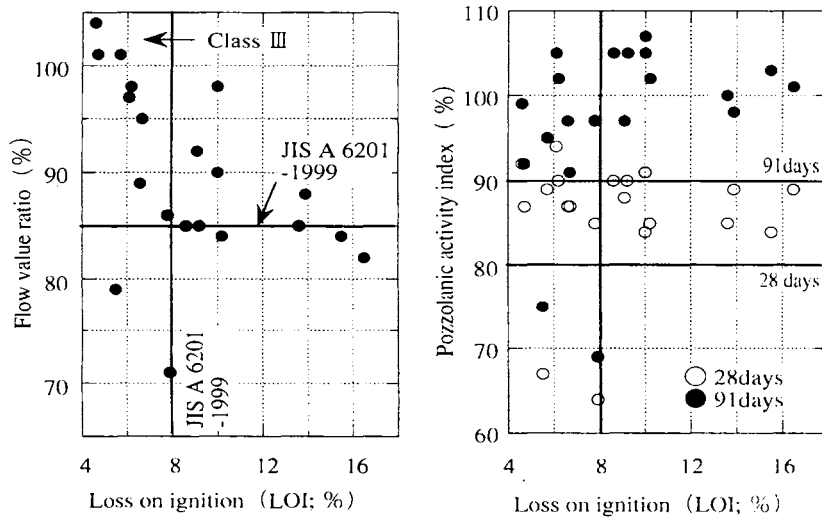


Fig.6 Relations among LOI, flow value ratio and pozzolanic activity index

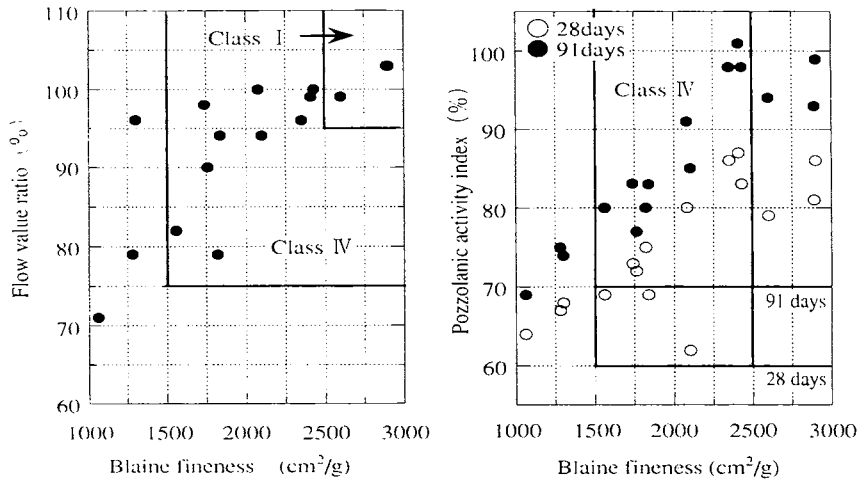


Fig.7 Relations among blaine fineness, flow value ratio and pozzolanic activity index

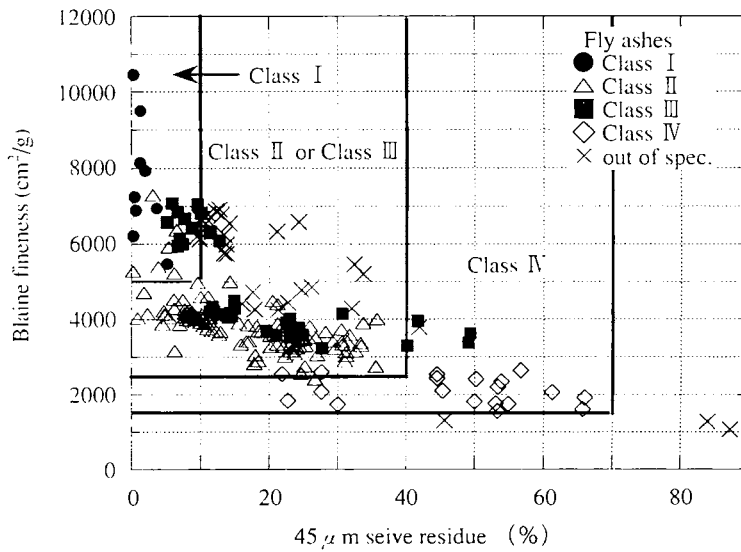


Fig.8 Relation between 45 μm sieve residue and blaine fineness

Effect of Chemical Activation of a Lagoon Ash on its Physico-Chemico-Mineralogical Properties

by P. K. Kolay and D. N. Singh

Synopsis: The amount of ash, produced from the coal fired thermal power plants and its hazardous impact on the environment is continuously increasing. This poses a challenging task of safe handling, proper disposal and utilisation of the ash. The huge quantity of ash produced from these power plants calls for a special attention in terms of its proper utilisation, either directly, or conversion into a value-added product. Chemical activation of the coal ash is being practised for synthesising ash zeolites. These zeolites are being used for various environmental protection schemes and other industrial processes. With this object in view, an effort has been made in this paper to study the effect of chemical activation of a typical class F lagoon ash. This chemical activation is achieved under controlled conditions, in the laboratory, with different concentrations of alkali (NaOH) and for different durations of activation.

Keywords: lagoon ash; synthesis; water-interaction; zeolites

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INTRODUCTION

Industrial development in any developing country needs a sustained supply of electrical energy. Major source of this electrical energy in India (as well as the world-wide) is the thermal power, constituting almost 70% of the total energy production, which is responsible for the production of enormous amount of ash from these power plants. Out of approximately 90,000 MW power generated in India, annually, more than 60,000 MW power is produced from the coal-based thermal power plants. These power plants generate almost 80 million tonnes of coal ash every year and the same is expected to increase to more than 100 million tonnes in the next few years. As such, this calls for a proper strategy for ash handling, disposal and utilisation. At present, only 5 to 10% of the ash is being used for various purposes viz., as a stabiliser of sub-grade and sub-bases in pavement construction, as a filling material for mines, as a constituents of cements, for treatment of polluted water and some agricultural soils, and to improve foundation soils.

Properties of the ash influencing its proper utilisation also depend on its handling, collection and storage. Another important aspect, which influences ash properties, is the method adopted for ash disposal, viz. dry or wet disposal. Though, dry disposal does not alter physical, chemical and mineralogical properties of the ash, the ash properties do change, to a great extent, when wet disposal of the ash is adopted. During the wet disposal as well as during storage, in the lagoons, the ash interacts with water and the alkalies present in it (Na_2O and K_2O) react with the major constituents of the ash (SiO_2 and Al_2O_3) to form different zeolites (1).

Some efforts have been made, in the recent past, to synthesise zeolites from the fly ash (2-8). These zeolites have been used in a variety of applications for preventing the degradation of the environment as well as for different industrial applications such as removal of heavy metals from the industrial sludge and flue gas, ammonia removal, replacement of phosphate in detergent, removal of radioactive waste, etc. However, researchers have not attempted the synthesis of zeolites from a lagoon ash. With this objective in view, a research study, as described in this paper, was undertaken to investigate the effect of chemical activation of a typical Class F lagoon ash, from India. The chemical activation was achieved under controlled conditions in the laboratory, with different alkali (NaOH) concentrations and for different durations of activation.

EXPERIMENTAL INVESTIGATION

Lagoon ash from Koradi Thermal Power Plant (KTPP) located at Nagpur, Maharashtra (India), was used for the present study. The ash sampling was done randomly from the slurry disposal site of the power plant. This ash sample is oven-dried and the same is termed as the Original Lagoon Ash (OLA). The OLA sample was treated with alkali (1N NaOH) for 24 hrs. in a water bath with reflux system. The treated ash sample is termed as the Activated Lagoon Ash (ALA). These ash samples (OLA and ALA) were characterised for their physical, chemical and mineralogical properties. Details of these tests are presented as follows:

Chemical composition

The chemical composition of the ash samples was obtained by using X-ray fluorescence (XRF) set-up (Model No. Phillips 1410, Holland).

Cation Exchange Capacity (CEC)

The CEC of the ash samples was determined according to IS: 2720 (Part XXIV, 1976). The ash sample is first treated with hydrogen peroxide (H_2O_2) and boiled thoroughly for 1 hr. to remove the organic contents of the ash. This ash is then oven-dried and a 5 g sample is taken to make a suspension of 50 ml 1N sodium acetate solution (pH=5). This suspension taken in a centrifuge tube is then digested in a boiling water bath for 30 min. (with intermittent stirring) and is centrifuged, at a speed of 5000 to 6000 rpm for 15

min. The supernatant liquid is discarded and the ash sample settled at the bottom of the tube is again treated with 50 ml of 1N sodium acetate solution (pH=5) and is centrifuged. This process is repeated thrice, so as to ensure exchange of Ca^{2+} in the ash sample by Na^{1+} . This ash sample is treated with 1N calcium chloride solution and is again digested and centrifuged as discussed above. This process is repeated thrice, so as to ensure exchange of Na^{1+} by Ca^{2+} . This ash sample is treated again with 50 ml 1N sodium acetate solution (pH=7) and is again digested and centrifuged as discussed above. This operation is performed thrice.

The amount of calcium present in the supernatant can then be estimated by titration against EDTA (Ethylene Di-amine Tetra Acetic acid) and the CEC (meq/100g of the ash) is calculated by using the following expression (9):

$$\text{CEC (meq/100g)} = \left(\frac{\text{Vol. of EDTA} \times \text{Normality of EDTA}}{\text{Wt. of the sample}} \right) \times 100 \dots \dots \dots [1]$$

Mineralogical composition

The ash samples have been evaluated for their mineralogical composition by using X-ray diffraction spectrometer (Phillips 2404, Holland) with a graphite monochromator and Cu-K α radiation. These samples were scanned from 2 θ ranging from 5 to 80°. The search match JCPDS data files were used for identification of the minerals present in these samples.

Scanning Electron Microscope (SEM)

The morphology of the ash samples was studied with the help of a Scanning Electron Microscope (JEOL, JSM 840A, Japan).

Grain size analysis

The gradational characteristics of the ash samples were obtained by dry sieving and by conducting sedimentation analysis with the help of a hydrometer (10).

Specific gravity

A series of tests have been conducted to determine the specific gravity of the ash samples (11).

Specific surface area

The specific surface area of the ash samples was determined with the help of Blaine's air permeability apparatus. For these tests, Portland cement has been taken as the standard material (its specific surface being 3460 cm²/g). The specific surface area (S) of the ash sample can be computed with the help of following equation:

$$S = [S_s(1-e_s)\sqrt[3]{T}/[\sqrt[3]{e_s}T_s(1-e)] \dots \dots \dots [2]$$

Where, S_s is the specific surface area of the Portland cement (=3460 cm²/g), e and e_s correspond to the void ratios of the ash and the cement (=0.5) samples, respectively. T_s and T are the times required by air to pass through the sample of cement (=77.18 sec.) and ash, respectively (12).

RESULTS AND DISCUSSION

The results of various tests, described above, conducted on the OLA and ALA samples, are being presented in the following:

The chemical composition (by % weight) of the OLA and ALA samples is presented in Table 1. It can be observed from the table that the major constituents of these samples are; silica (SiO₂), alumina (Al₂O₃) and ferric oxide (Fe₂O₃). Minor quantities of calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na₂O), potassium oxide (K₂O), sulphur oxide (SO₃) and other compounds are also observed to be present. These results indicate that the OLA belongs to Class F ash (ASTM, C-618) (13). The study reveals that alkali activation of the OLA causes a decrease in its silica content. In other words, the alkali activation causes dissolution of silica present in the ash sample.

The X-ray diffraction pattern of the OLA sample is presented in Fig. 1. To study the effect of alkali activation on this ash sample, diffraction pattern of the ALA sample has been superimposed in Fig. 1. From the figure it can be

noticed that quartz and mullite are the two crystalline phases most predominant in the OLA sample. However, as an effect of alkali activation of the OLA, these two phases lose their predominance and exhibit most predominant NaPl (zeolite) peak and hydroxy-sodalite phase.

The cation exchange capacity (CEC) of the OLA and ALA samples is found to be 100 and 244 meq/100g, respectively by using Eq. 1. The study indicates a two-fold increase in the CEC of the OLA sample due to its alkali activation. This may be attributed to the formation of NaPl and hydroxy-sodalite zeolites, in the ALA sample.

Figs. 2, 3 depict Scanning Electron Micrographs of the OLA and ALA samples, respectively. From the SEM studies on the OLA sample it can be observed that the OLA sample consists of different shapes of particles viz. spherical, hollow (cenosphere), broken, tubular and some other irregular shapes. However, in case of the ALA sample, some overgrowth on the surface of the ash particle takes place as a result of its alkali activation.

Physical properties of OLA and ALA samples are presented in Table 2. The average specific gravity values of the OLA and ALA samples are noticed to be 2.14 and 2.53, respectively. An increase in specific gravity of the ALA sample may be attributed to the fact that alkali activation results in etching of the ash particles which facilitates escape of the air (or moisture and gases) entrapped in its cenospheres. However, to ensure the effect of alkali activation on the OLA sample, another OLA sample was boiled in distilled water, without adding alkali, for almost 24 hrs and its specific gravity is determined. The same was noticed to be 2.18, which is almost equal to the average specific gravity of the OLA sample.

The specific surface area, obtained by using Eq. 2, of the OLA and the ALA samples is 1670 and 1860 cm²/g, respectively. It can be observed that the specific surface area of the OLA sample gets enhanced by almost 11%. This may again be attributed to the etching of the ash particles, due to alkali activation, which is responsible for exposing the inner surface of the cenosphere. Exposition of the inner surface results in an increased specific surface area of the OLA sample.

The gradational characteristics for the OLA and ALA samples are presented in Fig. 4. From the figure it can be noticed that the OLA consists of 55% sand (<4.75 mm), 41.5% silt (0.075-0.002 mm) and about 3.5% clay

(<0.002 mm). However, for the ALA sample the silt and sand fractions are noticed to be 45% and 55%, respectively. The study indicates that alkali activation of the OLA results in a decrease in its fine contents. These observations are consistent with the results of SEM studies (Figs. 2, 3).

CONCLUSIONS

Based on the experimental investigations conducted in the present study, on the original lagoon ash (OLA) and the alkali activated lagoon ash (ALA) samples, the following generalised conclusions can be drawn:

Alkali activation causes a decrease in silica content of the lagoon ash. It has also been observed that alkali activation is responsible for etching (and hence dissolution) of the silica present in the ash.

Alkali activation of the OLA results in an increase in its specific gravity by almost 25%. The specific surface area of the OLA sample is noticed to increase by more than two-folds which may be attributed to the etching (as well as dissolution) of silica present in the ash.

Formation of NaPl and hydroxy-sodalite zeolites has been noticed. This has also been confirmed by cation exchange capacity values obtained for the OLA and ALA samples. This indicates potential of alkali activated lagoon ash for its use in various environmental protection schemes, viz. heavy metal removal/retention, from the industrial sludge, for treatment of polluted water and agricultural soils.

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Table 1. Chemical composition (by % weight) of the OLA and ALA samples

Oxides	OLA	ALA
SiO ₂	59.89	54.01
Al ₂ O ₃	27.20	24.11
Fe ₂ O ₃	4.33	6.391
CaO	1.01	0.948
SO ₃	1.53	0.032
Na ₂ O	0.06	0.063
K ₂ O	0.93	0.698
MgO	0.08	0.380
TiO ₂	2.30	2.128
P ₂ O ₅	0.23	0.137
L.O.I.	2.44	11.11

L.O.I. : Loss on ignition.

Table 2. Physical properties of the OLA and ALA samples

Properties	OLA	ALA
Specific gravity	2.14	2.53
Specific surface area (cm ² /gm)	1670	1860
<u>Gradational characteristics (%)</u>		
Sand (<4.75 mm)	55.0	55.0
Silt (0.075-0.002 mm)	41.5	45.0
Clay (<0.002 mm)	03.5	0.0