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**ENVIRONMENTAL CHARACTERISTICS OF SOLID WASTE STREAMS
FOR TRANSITIONAL TECHNOLOGIES**

RESEARCH REPORT 89

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CONTENTS

EXECUTIVE SUMMARY 4

INTRODUCTION 5

Fluidised bed combustion..... 6

Oxyfuel combustion..... 7

Integrated Gasification Combined Cycle (IGCC)..... 7

EXPERIMENTAL 12

RESULTS..... 12

Assessment of the Material from the FBC Plants 12

Investigation of the IGCC Slags..... 23

ACKNOWLEDGEMENTS 32

REFERENCES..... 32

APPENDIX 1. COMPARISON OF THE LEACH DATA ON THE ASHES FROM THE FBC PLANTS..... 35

APPENDIX 2. COMPARISON OF THE LEACH DATA ON PAIRED ASHES FROM THE AIR-FIRED AND OXY FUEL COALS 47

APPENDIX 3. COMPARISON OF LEACH DATA FROM GASIFIER SLAGS..... 53

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EXECUTIVE SUMMARY

This report is an evaluation of the differences between the waste products of transitional power generation technologies and the fly ash (and bottom ash) produced by conventional pulverised fuel power stations. Any such differences may indicate that there are advantages associated with environmentally sound disposal of the waste streams from such technologies, or alternatively that transitional wastes may have deleterious properties that might impact adversely on the options for their disposal. The three transitional technologies for the utilisation of coal in electricity generation considered in this report are:

- Fluidised bed combustion (FBC)
- Oxyfuel combustion
- Integrated Gasification Combined-Cycle (IGCC. using slagging gasifiers).

Samples of the major residues (ash or slag) were obtained from plants or pilot plants using Australian coal as feeds in each of the transitional technologies. The samples were analysed using the protocol previously developed in other CCSD leaching studies on fly ash from conventional pulverised fuel power stations. The following materials were investigated:

- Fluidised bed combustion residues - samples of silo ash (fly ash) and bottom ash (bed material) from a power station in Australia and the Karita Power Station in Japan.
- Oxyfuel combustion ashes - three pairs of ash samples from air-fired and oxy-fuel combustion tests conducted on Queensland coals by CS Energy.
- Coal feeds – the coal feeds used in the oxy fuel trials were also analysed and relevant analytical data reported.
- IGCC slags – five samples obtained from trials completed at the Siemens' test facility in Germany on Australian coals. As well as these samples, a gasifier slag from an Australian coal processed in the Buggenum Plant, The Netherlands was also evaluated.

Based on the analytical data obtained in this project, and bearing in mind that only limited samples of ash and slag from the transitional technologies were available, it was concluded that:

- Most trace elements were leached from the fly ash and bottom ash of FBC systems at similar concentrations to those present in the leachate of ash from conventional power stations (i.e. using coal fired as pulverised fuel in air), although there are possibly some exceptions. Lower concentrations of Cd, Co, Ni and Zn were found in the leachates of the ash from the Australian and Karita FBC power stations compared to typical pf materials.
- Trace elements were leached in similar proportions from fly ashes derived from the same coal fired respectively in conventional and oxy-fuel combustion conditions; indeed there does not appear to be any significant differences in the leaching behaviour of trace elements in the ashes from equivalent coals fired in these two different systems. Some of the trace elements in the gasifier slags were not leached as readily as those in the fly ash from conventional power stations; these trace elements are B, Cr, Mn, V and Zn and possibly Co and Cu. However, there does not appear to be any change in the leachability of the other trace elements, including As and Se. Certainly, IGCC slag has a larger particle size and has less surface area in contact with a leach solution than pf ash and although it is sometimes claimed that slag from IGCC plants “is environmentally benign and can be safely landfilled”, obviously care must be taken with its disposal as there are still likely to be trace elements that may be leached.

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INTRODUCTION

Currently, Australia produces approximately 10 million tonnes per annum of pf-combustion wastes (or combustion products) from coal-fired power stations. A small proportion is utilised, but most is deposited in wet ash dams or dry repositories. Interestingly, Morrison et al. (2005) consider that one outcome of a change in the mix of electricity generating plant in Australia is the likely halving of the availability of fly ash by 2050. The change in the mix would be a consequence of constraints on the emission of CO₂ and the adoption of transitional technologies.

The three transitional technologies for the utilisation of coal in electricity generation considered in this report are:

- Fluidised bed combustion (FBC)

Fluidised bed combustion is a system in which the fuel (e.g. coal) is fed into a solid bed, which has been fluidised by upward movement of air. FBC can be operated at atmospheric pressure (AFBC) or at elevated pressures (PFBC). Such systems offer advantages including simple construction and flexibility in use of fuel types as well as their high combustion efficiency at a low temperature (750-950°C). A major advantage is the ability to remove SO₂ using added limestone or dolomite in the bed material (see description in IFRF Online Combustion Handbook, <http://www.handbook.ifrf.net/handbook/index.html>).

- Oxyfuel combustion

Oxyfuel combustion is the combustion of coal in an atmosphere of carbon dioxide and oxygen. This differs from the usual process in which pulverised coal is burnt in air (primarily nitrogen and oxygen). The combustion products of the combustion in air are in the main nitrogen, residual oxygen and carbon dioxide whereas those from oxyfuel combustion are carbon dioxide and oxygen. Thus the oxyfuel process requires the replacement of air with a mixture of oxygen and recirculated waste gases; the result is a concentrated stream of carbon dioxide that can more readily be captured and ultimately sequestered. In Australia, CS Energy is actively working on the development of this process. http://www.csenergy.com.au/research_and_development/oxy_fuel.aspx

- Integrated Gasification Combined-Cycle (IGCC) using Slagging Gasifiers:

In a gasifier, the solid fuel (coal in this case) is pyrolysed in limited air or oxygen to produce syngas, primarily hydrogen and carbon monoxide. The development of slagging gasifiers for Australian coals is a major part of the CCSD research program. In these gasifiers, most of the mineral material melts to produce a slag. However, a small fraction of the mineral matter reacts to form fly ash; this is removed by filtration (hot gas cleaning) from the gasification products. In IGCC systems, the cleaned syngas (i.e. after removal of hydrogen sulfide, ammonia and particulate matter) is burned in a combustion turbine to produce electricity. Hot exhaust air from the combustion turbine can be channelled back to the gasifier or the air separation unit; the exhaust heat is used to generate steam for a conventional steam turbine-generator.

These technologies are discussed in a number of recently released reports into the future of coal (see Rardin, 2005; MIT, 2007). Also see the report by Minchener and McMullan, (2007) on the research on clean coal technologies in the EU.

The major solid waste streams from each of these (transitional) processes are respectively:

- fly ash, ash and fluidised bed material
- fly ash and bottom ash ash generated in an atmosphere of carbon dioxide and oxygen
- slag produced in an atmosphere depleted of oxygen (some fly ash but this is likely to be recycled to produce slag).

The major solid waste stream from the coal-fired generation of electricity in Australia is currently fly ash, but it may be replaced by IGCC slag in the future. Morrison et al. (2005) state “development of high tonnage end use strategies for IGCC [slag] is required if coal in the near-zero emissions strategies

is to contribute to a more sustainable society". Adams (2004) has reported on the opportunities and difficulties for the use of residues from both FBC and IGCC plants; the comment is made that the residues being a secondary product of energy production, have few controls on their generation and thus there is variation in their properties.

The aim was to evaluate the differences between these transitional waste products and the fly ash (and bottom ash) produced by conventional coal-fired power stations. Any such differences may indicate advantages associated with the environmentally sound disposal of the waste streams from transitional technologies, or alternatively that transitional wastes may have deleterious properties that impact adversely on the options for their disposal.

Fluidised bed combustion

This technology includes systems such Atmospheric Fluidised Bed Combustion (AFBC), Circulating Fluidised Bed Combustion (CFBC), Pressurised Fluidised Bed Combustion (PFBC), Pressurised Circulating Fluidised Bed Combustion (PCFBC).

Although it has been claimed in one report on the use of the waste materials in the manufacture of building materials (Ehrnsperger and Misch, 2006) that "There is no substantial difference between fly ash from fluidised-bed furnaces and from slag-tap furnaces", it is obvious from an environmental aspect that the nature of the residues from a FBC plant will differ from those from a PC plant. For example, the lower combustion temperature may result in a lowering of the concentrations of some trace elements in the fly ash. Conversely, in such cases, the concentration of the same trace elements would be higher in the fluidised bed material (i.e. residual ash and bed material e.g. calcium carbonate/oxide and calcium sulphate) and this may be a significant consideration in the disposal of the waste product (see Armesto and Merino, 1999; Demir et al., 2001; Benito et al., 2001). Note that Ehrnsperger and Misch (2006) have used the abbreviation "PC" for pulverised coal.

In a study of the mobilisation of trace element mobilisation from a fluidized bed combustion (FBC) plant, a pulverised coal combustion (PC or PF) plant, and a cyclone (CYC) plant in Illinois, Demir et al. (2001) concluded that the mobilities of the 15 trace elements investigated were lower at the FBC plant than at the other plants. There are obvious differences in the behaviours of individual trace elements as only F and Mn at the FBC plant and F, Hg, and Se at the PC plant "had over 50% of their concentrations mobilized". Of the other trace elements studied Cd was reported as having medium mobility in the FBC plant compared with Co, Mn, Ni and U in the PC plant.

Although trace element emissions from FBC units may be lower than those arising from pf combustion, the element concentrations in the solid residue may be higher and thus there is concern about their possible leaching behaviour. The higher calcium and magnesium contents of FBC ash and the possible different mode of occurrence of trace elements and ash mineralogy due to the lower combustion temperatures experienced may also have implications for disposal and utilization of FBC residues. There is an early report on PFBC by Nilsson and Clarke (1994) in which the authors make the observation that "PFBC systems offer advantages over other coal utilisation technologies in terms of environmental performance, fuel flexibility, and overall efficiency. However, these systems produce large quantities of residues, with properties that differ from the residues discharged from pulverised coal combustion or atmospheric fluidised bed combustion. The residues are a mixture of ash from the coal and sorbent derived materials. Results indicate that most PFBC residues would be classified as non hazardous under existing legislation. Many utilisation options have been suggested for PFBC residues. At present the most favourable uses appear to be in structural fills or soil stabilisation applications. Utilisation of PFBC residues is hampered by the limited quantities of residues produced from the few commercial scale plants." See also the report by Takeshita (1994) on the environmental performance of coal-fired FBC technology - elevated emissions of N₂O and the management of residues "are the major disadvantages". Solem-Tishmack. and McCarthy (1995) also make the observation that combustion products high in calcium (as in FBC systems where limestone is used) may facilitate the formation of ettringite which can bind trace elements such as Se in an insoluble phase.

Although the FBC system is defined as a transitional technology, the question remains as to whether this technology will be in the mainstream of coal combustion technologies or whether it will be a niche “low emissions” technology for the utilisation of waste material (some of which will be coal wastes) and biomass. However it is considered in this report.

Oxyfuel combustion

There does not appear to be much literature on the subject of trace element behaviour when coal is combusted in an oxyfuel system. It is possible (even likely) that the trace elements will partition in much the same way as trace elements do in conventional pf power stations (see Clark and Sloss, 1992). Thus the trace elements will partition according to the definitions used by Meij (1994) and also Sloss and Smith, (2000) i.e.

Class I - least volatile and remain in the ash residues i.e. Eu, Hf, La, Mn, Rb, Sc, Sm, Th, Zr and also Ba, Be, Bi, Co, Cr, Cs, Cu, Mo, Ni, Sr, Ta, Tl, U, V and W (this latter group of elements have some volatility)

Class II - more volatile and partition between the residual ash and the gaseous phase, with condensation of vaporized species on the surface of ash particles i.e. As, Cd, Ga, Ge, Pb, Sb, Sn, Te, Ti, Zn and also B, Se and I (again this latter group of three exhibit greater volatility than the others in this Class).

Class III - highly volatile and show little or no tendency to condense from the vapour phase i.e. Hg as well as Br, Cl and F.

As from air-fired pf systems, the major solid waste from an oxyfuel system is fly ash (80%-90%) with a corresponding proportion of bottom ash.

Integrated Gasification Combined Cycle (IGCC)

Unlike conventional pf, oxyfuel and FBC systems, the bulk of solid waste from most IGCC plants is slag (regarded as environmentally benign, see below). However a minor proportion of fly ash is also generated. This is removed by the hot gas cleaning system prior to the gas stream reaching the gas turbine. Although most of the current gasifier projects are based upon slagging gasifiers which produce a glassy slag and small amounts of fly ash, there are other systems (e.g. the moving-bed gasifiers used in South Africa). The waste streams of the various gasifier technologies are presented in Table 1, along with other process characteristics.

Pflughoeft-Hassett, (1997) states the most “prominent coal gasification processes incorporated into IGCC, such as ChevronTexaco, E-Gas and BGL, are slagging systems that operate at high pressure. Therefore, most ash is in the form of slag, which can be likened to wet-bottom pulverized coal boiler slag. While the amount of fly ash varies according to the type of gasification process, it is often recycled to consume the char and minimize the quantity of fly ash produced. Therefore, the ratio of slag or bottom ash to fly ash is usually much higher in IGCC plants than it is in combustion based plants.This large difference in fly ash quantities is an advantage for coal gasification because fly ash is more difficult to handle, use, and dispose of than bottom ash or slag.”

Table 1. Characteristics of gasifier technologies (Ratafia-Brown et al., 2002a).

| GASIFIER TYPE | MOVING-BED | | FLUIDIZED-BED | | ENTRAINED-FLOW |
|---------------------------------------|---|--|---|---|--|
| | Dry Ash | Slagging | Dry Ash | Agglomerating | |
| Ash Conditions | Dry Ash | Slagging | Dry Ash | Agglomerating | Slagging |
| FUEL CHARACTERISTICS | | | | | |
| Fuel size limits | 6-50 mm | 6-50 mm | <6 mm | <6 mm | <0.1 mm |
| Preferred fuel | Lignite, reactive bit. coal, anthracite, wastes | Bit. coal, anthracite, petcoke, wastes | Lignite, reactive bit. coal, anthracite, wastes | Lignite, bit coal, anthracite, cokes, biomass, wastes | Bit. coal, anthracite, petcokes, oil residues etc |
| Ash content limits | No limit | <25% preferred | No limit | No limit | <25% preferred |
| Preferred ash melting temperature, °C | >1200 | <1300 | >1100 | >1100 | <1300 |
| WASTE STREAM | | | | | |
| Ash Type | Dry ash | Slag | Dry ash | Agglomerated dry ash | Slag |
| Particulates | Recycled | None | Process dependent Recycled/filter cake | Process dependent Recycled | Process dependent Recycled/filter cake/dry residue |

Duffy and Nelson (1997) have reviewed the literature up to that year on the behaviour of emissions from IGCC plants. Helble et al. (1996) have estimated the partitioning of trace elements during gasification. The researchers used thermodynamic calculation and measurements obtained on a laboratory scale reactor to obtain the data. Perhaps not surprisingly, high proportions (>20%) of the elements, As, Cd, Sb, Se and Zn were reported as volatile. Font et al. (2004) determined the concentration and speciation of a number of trace elements in flyash from an IGCC unit (Puertollano, Spain). Note that these studies relate to the behaviour of trace elements in the fly ash generated during gasification; however, unlike conventional pf-fired plants, the ash will be a minor waste stream of IGCC. Also some IGCC units are utilising both coal and petroleum coke (the latter often contains high concentrations of sulfur, nickel and vanadium), so that caution must be exercised in comparing the data.

Some gasifier systems are also being used to co-fire with waste or biomass material but according to Jenkins (2006), “fly ash and bottom ash from coal-fired plants has exclusion from RCRA Subtitle C as a fossil fuel combustion waste whereas slag from coal gasification is covered as a mineral processing waste, if feedstock is >50% coal”. If <50% coal, then it is a requirement that “the slag passes appropriate tests to show it is not hazardous.” See www.netl.doe.gov/technologies/coalpower/gasification/pubs/tampa-2006/Jenkins.pdf. Also see the reports of NETL (2000; 2002) on the Tampa and Wabash gasifiers. Ratafia-Brown et al. (2002a) state “Emissions of trace inorganic and organic hazardous air pollutants (HAPs) are extremely low, comparable with those from coal combustion-based plants that use advanced emission control

technologies.The ash (slag or bottom ash) and sulfur (or sulfuric acid) generated by operating IGCC plants have been tested to be environmentally benign and can be sold as valuable by-products.” Table 2 (below) has been extracted from that report (see also Ratafia-Brown et al., 2002b).

Table 2. Comparison of Trace Element Concentrations in PF Slag and Gasifier Slag (Ratafia-Brown et al., 2002a).

| Element | PF (coal) Boiler Slag | | Gasification Slag |
|-----------|-----------------------|----------|-------------------|
| | Mean | Range | Range |
| | mg/kg | mg/kg | mg/kg |
| Antimony | 0.7 | 0.25-1.0 | 5-<10 |
| Arsenic | 23 | 0.01-254 | 6-<10 |
| Barium | 700 | 6.2-1720 | 38-80 |
| Beryllium | 7 | 7.0-70 | 2-11 |
| Boron | 32 | 0.1-55 | 128-283 |
| Cadmium | 22 | 0.01-40 | <50-0.8 |
| Chromium | 592 | 1.4-5980 | 30-120 |
| Copper | 52 | 1.4-156 | 12-54 |
| Lead | 35 | 0.4-120 | 8-97 |
| Mercury | 5 | 0.02-9.5 | <0.08 |
| Nickel | 81 | 3.3-177 | 23-147 |
| Selenium | 5 | 0.01-14 | <10 |
| Silver | 22 | 0.01-74 | <1-3 |
| Thallium | 37 | 34-40 | <0.4-16 |
| Vanadium | 146 | 75-320 | 25-156 |
| Zinc | 79 | 4.4-530 | 33-213 |

It is important to note that the data are comparisons between pf boiler slag (i.e. bottom ash) and the gasifier slags. The concentrations of trace elements in the fly ash from pf units would be higher than in boiler slag in most cases. It is important to also note that some of these data appear to be highly unusual. In particular, the upper level of concentrations of As and Cr for the pf slag are extremely high as are the concentrations of Tl. Also important is the comment in this report that TCLP leachates of gasifier slags contain much lower concentrations of trace elements than found in the leachates of pf slags.

Although there are many articles and reports on the use of fly ash from conventional PC (or PF) power stations (for example, see Sloss, 2007) and on the management of ash in such plants (see Couch, 2006), there are few reports on the ash or slag from the transitional technologies. There are even fewer reports in which there are some comparisons of pf systems and the transitional systems, although there are some. For example, Pflughoeft-Hassett (1997) has compared FBC and IGCC systems and comments that “If a trace element is primarily captured within the slag, then it is essentially permanently sequestered and poses very little environmental threat.Elements that partition to IGCC solid residue streams will primarily impact the environment and health via leachability.”

Table 1-9 in Ratafia-Brown et al. (2002a, pp 1-29) illustrates the comparison of waste streams from IGCC, PF and FBC systems. This table, reproduced as Table 3 (below), provides a concise summary

of the waste streams from transitional technologies fueled by coal for the generation of electricity. Although there is no comparison of oxyfuel systems in the table and there is little such information available, it is likely that oxyfuel combustion will produce waste streams (in particular fly ash), that behave very similarly to those produced in conventional pf power stations (although the behaviours of some trace elements in the oxyfuel fly ashes may differ those from typical pf fly ash).

Ratafia-Brown et al. (2002a) make the observation on the emissions and the partitioning of the trace elements in coal from PC (i.e. PF), PFBC (no data from AFBC) and IGCC systems that “this is a difficult comparison to make based on the limited data available, the inherent limitations of the sampling and analytical protocols, and the different testing organizations involved. However, generally, the results of this comparison indicate that trace metal emissions are quite low for all technologies, and that IGCC emissions appear to be comparable to other well-controlled coal-fueled power plants.” Clarke and Sloss (1992) also compare the emissions of trace elements from coal combustion and gasification.

In this CCSD project the environmental availability (i.e leachability) of the trace elements from the major solid wastes produced by each of these technologies has been addressed. No attempt has been made to assess the overall partitioning of trace elements in pf, oxyfuel, FBC and IGCC systems.

Table 3. Comparison of Solid Waste Streams from PF, FBC and IGCC Plants (Ratafia-Brown et al., 2002a).

| | PF (Coal) Plant | FBC Plant | IGCC Plant |
|----------------------------------|--|---|--|
| Particulate Matter Control | Very high levels of particulate control. Fly ash is efficiently collected in a control device, such as an ESP or fabric filter. Acid mist may be problem from FGD unit. | Very high levels of particulate control. Ash and spent sorbent (limestone) is collected in a control device such as a cyclone. Usually primary and secondary particulate control devices. No acid mist problem. | Virtually all particulate is removed. Fly ash entrained with syngas is removed downstream in wet scrubber.No acid mist problem. |
| Trace Substance Control | Most semi-volatile and volatile trace metals condense on fly ash particles and are effectively removed with fly ash. Elemental mercury emissions may exit with flue gas. Other elements exit with ash and FGD byproduct. Trace organic emissions are extremely low. Hg emissions may depend on coal type and presence of FGD system. | Most semi-volatile and volatile trace metals condense on fly ash particles and are effectively removed with ash. Elemental mercury emissions may exit with flue gas. Other elements exit with calcium-sulfate-based ash. Trace organic emissions are extremely low. Hg emissions may depend on coal type. | Most semi-volatile and volatile trace metals condensed and removed in syngas cleaning equipment. Elemental mercury emissions may exit with flue gas. Other metals exit with wastewater blowdown and wastewater treatment material. Trace organic emissions are extremely low. Activated carbon beds have been commercially demonstrated to remove more than 90% of syngas mercury. |
| Solid Waste Disposal/Utilization | Bottom ash and fly ash can be safely landfilled. Leaching of trace metals adsorbed by fly ash is more likely than with slag material. Ash can beutilized for a variety of applications, such as cement/concrete production and waste stabilization /solidification. | Calcium-sulfate-based ashes are chemically stable and are easily disposed. Leaching of trace metals adsorbed by fly ash is more likely than with slag material. This ash can be used as raw material for cement manufacturing, soil stabilization, concrete blocks, roadbase, structural fills, etc. | Slag material is environmentally benign and can be safely landfilled. Slag can also be safely utilized for various applications, such as drainage material or roofing granules. Similar to material produced by wet-bottom PC plants. |

EXPERIMENTAL

Samples of the major residues were obtained from plants or pilot plants using coal as feeds in each of the transitional technologies discussed in the preceding section. The samples were analysed and also extracted with MilliQ water to obtain data that could be compared with previous CCSD leach studies on fly ash from conventional pulverised fuel (coal) fired power stations. In brief, the samples of residues (ashes or slags) were leached for three days in distilled water at liquid:solid ratios of 3.5:1 and 20:1. The leach procedure follows that described by Ward et al. (2007) and is based on earlier CCSD research described by Jankowski et al. (2004; 2006). The leachates were filtered through 0.22 µm Millipore cellulose acetate membrane filters. An unacidified portion of the filtrates was analysed for pH and conductivity. Another portion of the filtrate was acidified to approximately 1% v/v AR grade concentrated nitric acid and the concentrations of trace elements determined using ICP-AES and ICP-MS.

As well as the leach tests, the chemical and mineralogical compositions of the ash and slag products were also determined by X-ray fluorescence spectrometry (XRF) and X-ray diffractometry (XRD). The samples also analysed for a number of trace elements using a variety of different techniques.

The following materials were investigated:

- Fluidised bed combustion residues - samples of silo ash (fly ash) and bottom ash (bed material) from both the power station in Australia and the Karita Power Station in Japan.. The samples from Australia are identified as RSA and RBA; those from Karita are identified as KFA and KBA.
- Oxyfuel combustion ashes – pairs of ash samples from air-fired and oxyfuel combustion tests conducted on three Queensland coals by CS Energy.
- Coal feeds – the ash and mineral matter for the coal feeds used in the oxy fuel trials were also analysed and the analytical data reported
- IGCC slags – these were obtained from trials completed at the Seimens' test facility in Germany on Australian coals identified as CRC701, CRC702, CRC703 and CRC704; the latter two coals are from the same mines that supplied samples for the original CCSD “coal bank”, i.e. CRC272 and CRC281 respectively. Note that, for the gasifications trials, coal CRC703 was mixed with flux. The slag samples are identified as Tests 100 and 101 using CRC701, Test 102 using CRC702, Test 103 using CRC703 and Test 104 using CRC704. The received slag samples were air dried before analysis and the leaching tests. As well as these samples, a gasifier slag (identified as “Bugg”) from the Buggenum Plant, The Netherlands was also included in the study. The samples were also photographed (Fig. 1).

RESULTS

The results obtained from the analyses of the transitional waste products and also those obtained from the leach tests are considered in this section. These are compared with the data obtained on fly ash from the same or similar coals combusted in conventional pf-fired power stations in the following section.

Assessment of the Material from the FBC Plants

The inorganic phases (determined by XRD) in the materials from the two FBC plants (in Australia and Karita) are given in Table 4. Note that the interpretation of the diffraction pattern obtained by XRD of the Karita bottom ash (KBA) was extremely difficult. In this material, there was little apparent amorphous material present and there is a possibility that phases other than those identified are present.

Table 4. Inorganic Phases in Ashes from FBC Plants

| | Silo ash | Bottom ash | Fly ash | Bottom ash |
|---------------------------|----------|------------|---------|------------|
| | RSA | RBA | KFA | KBA |
| Phase (wt %) | | | | |
| Quartz | 25.8 | 30.0 | 3.7 | 9.8 |
| Mullite | 0.9 | 2.3 | 6.1 | |
| Hematite | 1.0 | 1.9 | | |
| Maghemite | 0.7 | 0.6 | 1.0 | |
| Magnetite | 0.3 | 0.2 | | |
| Anorthite | 0.7 | 3.7 | 11.8 | 4.4 |
| Calcite | 1.6 | 0.9 | 3.1 | 43.6 |
| Portlandite | | 4.2 | 0.6 | 2.6 |
| Anhydrite | 0.4 | 1.2 | 7.5 | 5.8 |
| Lime | | | 3.0 | 16.7 |
| Gehlenite | | | 8.5 | 6.3 |
| Merwinite | | | 6.6 | 5.0 |
| Periclase (?) | | | 0.7 | |
| Melilite, sodic | | | 5.8 | 5.7 |
| Gypsum | 3.0 | | | |
| Amorphous (as metakaolin) | 65.5 | 54.8 | 41.6 | |

The compositions (major elements by XRF) of the materials are reported in Table 5. The concentrations of the trace elements are reported in Table 6.

Table 5. Analyses of Ashes from FBC Plants

| Sample | RSA | RBA | KFA | KBA |
|--------------------------------|------------|------------|------------|------------|
| % | | | | |
| C | 8.1 | 0.4 | 4.5 | 3.0 |
| S | 0.8 | 0.4 | nd | nd |
| Al ₂ O ₃ | 20.6 | 23.6 | 7.90 | 20.1 |
| CaO | 3.74 | 6.37 | 46.9 | 32.2 |
| Fe ₂ O ₃ | 4.29 | 4.05 | 1.71 | 3.50 |
| K ₂ O | 1.20 | 1.66 | 0.53 | 0.43 |
| MgO | 0.61 | 0.77 | 1.34 | 2.02 |
| MnO | 0.05 | 0.04 | 0.04 | 0.05 |
| Na ₂ O | 0.23 | 0.09 | 0.72 | 0.95 |
| P ₂ O ₅ | 0.41 | 0.11 | 0.13 | 0.29 |
| SiO ₂ | 51.8 | 58.8 | 18.8 | 27.6 |
| SO ₃ | 1.70 | 0.70 | 4.12 | 6.28 |
| TiO ₂ | 0.80 | 0.57 | 0.35 | 0.97 |
| LOI | 14.0 | 2.5 | 14.8 | 6.0 |
| Total | 96.8 | 98.7 | 82.5 | 100.3 |

(nd: not determined; low recoveries are expected from combustion techniques i.e. Leco instrumentation used)

Table 6. Concentrations of Trace Elements in FBC Ashes

| Sample | RSA | RBA | KFA | KBA |
|---------------|------------|------------|------------|------------|
| mg/kg | | | | |
| As | 3.02 | 0.63 | 3.9 | 7.6 |
| B | 320 | 37 | 120 | 403 |
| Ba | 469 | 256 | 390 | 1500 |
| Be | 5 | 1 | 1 | 5 |
| Bi | 0.2 | 0.2 | 0.2 | 0.9 |
| Cd | 0.11 | 0.06 | 0.5 | 0.9 |
| Cl | 240 | 150 | 400 | 770 |
| Co | 25 | 9 | 32 | 32 |
| Cr | 121 | 84 | 35 | 67 |
| Cu | 40 | 20 | 21 | 94 |
| F | 970 | 110 | 244 | 371 |
| Hg | 0.14 | <0.02 | 0.01 | 0.07 |
| Mo | 0.7 | 0.5 | 2.3 | 12 |
| Ni | 83 | 5 | 28 | 52 |
| Pb | 43 | 32 | 28 | 45 |
| Sb | 0.37 | 0.26 | 0.6 | 1.9 |
| Se | 1.98 | <0.1 | 3.0 | 48 |
| Sr | nr | nr | 540 | 1600 |
| Th | 16 | 24 | 7.8 | 27 |
| U | 9 | 6 | 1.7 | 6.3 |
| V | 148 | 63 | 49 | 160 |
| W | 1.1 | 0.5 | <0.1 | 2.2 |
| Zn | 100 | 86 | 12 | 46 |

The analyses of the leachates of the ashes from the Australian and Karita FBC plants are reported in Table 7. The designations “35” and “20” refer to leachates obtained at liquid:solid ratios of 3.5:1 and 20:1 respectively.

Table 7. Analyses of Leachates of Ashes from FBC Plants (l:s ratios = 3.5:1 & 20:1)

| | RSA-35 | RBA-35 | RSA-20 | RBA-20 | KFA-35 | KBA-35 | KFA-20 | KBA-20 |
|-----------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| pH | 8.3 | 12.4 | 8.6 | 12.4 | 12.3 | 12.3 | 12.2 | 12.3 |
| Condy* | 2.38 | 8.64 | 1.38 | 8.24 | 7.37 | 9.25 | 6.83 | 8.95 |
| mg/L | | | | | | | | |
| B | 2.0 | <0.2 | 0.4 | <0.2 | 0.2 | 0.4 | 0.3 | 0.8 |
| Ca | 624 | 1010 | 322 | 872 | 610 | 1386 | 621 | 979 |
| Fe | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| K | 12.0 | 60.6 | 4.0 | 12.2 | 39.6 | 3.9 | 6.0 | 0.8 |
| Mg | 8.6 | <0.1 | 1.9 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Na | 5.4 | 12.9 | 1.4 | 2.7 | 55.7 | 4.4 | 9.4 | 1.1 |
| SO₄ | 1523 | 684 | 779 | 265 | 19 | 1578 | 20 | 365 |
| Si | <5 | <5 | <5 | <5 | <5 | <5 | <5 | <5 |
| g/L | | | | | | | | |
| Al | 265 | 2.0 | 499 | 1.7 | 973 | 50 | 1392 | 5 |
| As | 2.5 | 0.7 | 2.1 | 0.6 | 0.2 | 1.6 | 0.3 | 0.9 |
| Ba | 77 | 345 | 103 | 268 | 37048 | 105 | 12067 | 270 |
| Cd | 0.65 | 0.44 | 0.12 | 0.13 | 0.13 | 0.11 | 0.12 | 0.05 |
| Co | 1.74 | 1.44 | 0.58 | 1.13 | 0.8 | 1.6 | 0.8 | 1.2 |
| Cr | 2.49 | 22.91 | 1.83 | 8.63 | 9 | 92 | 7 | 37 |
| Cu | 0.41 | 0.88 | 0.22 | 0.56 | 2.16 | 0.86 | 1.41 | 0.68 |
| Li | 15 | 44 | 8.3 | 16 | 9218 | 402 | 1322 | 82 |
| Mn | 10 | <0.1 | 4 | <0.1 | <0.1 | 1649 | <0.1 | 2118 |
| Mo | 295 | 184 | 52 | 50 | 66 | 52 | 48 | 22 |
| Ni | 0.7 | 1.5 | 0.4 | 1.0 | 1.4 | 2.7 | 1.1 | 2.8 |
| Pb | <0.1 | 1 | <0.1 | 1 | 8 | 2 | 8 | 2 |
| Sb | 5.52 | 0.01 | 2.22 | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Se | 55.5 | 1.3 | 12.0 | 1.0 | 42 | 61 | 37 | 13 |
| Sr | 7469 | 4500 | 3464 | 1535 | >> | 16109 | 15830 | 4005 |
| Th | <0.1 | <0.1 | -0.02 | -0.03 | 0.00 | 0.02 | -0.01 | 0.00 |
| U | 2.6 | <0.1 | 0.8 | <0.1 | <0.1 | 0.1 | <0.1 | <0.1 |
| V | 190 | <1 | 125 | 1.0 | <1 | <1 | <1 | <1 |
| W | 22 | 0.5 | 6.9 | 0.7 | 0.20 | 0.15 | 0.25 | 0.11 |
| Zn | 10 | 8.5 | 8.5 | 7.5 | 16 | 11 | 11 | 8.7 |

(* mS/cm; >>: over range)

Comparison of Ashes from Air-fired and Oxy Fuel Coals

Samples of coals and ashes from combustion under normal conditions and under oxy fuel conditions in an experimental combustion rig were studied. The mineralogical phases in the coals used in air-fired and oxy-fired tests are given in Table 8.

Table 8. Inorganic Phases in Coals used in Air-fired and Oxy Fuel Tests

| | Acland Coal | Callide Coal | Rolleston Coal |
|-----------------------|----------------------------|-------------------------|---------------------------|
| | | % | |
| Mineral Matter | 21.1 | 26.6 | 7.8 |
| Phase | % of Mineral Matter | | |
| Anatase | 0.4 | 1.3 | 1.4 |
| Bassanite | 0.3 | 1.5 | 6.0 |
| Brookite | 0.5 | | |
| Calcite | 0.1 | 0.2 | 0.4 |
| Chamosite | | | 1.5 |
| Fluorapatite | 0.1 | | 2.5 |
| Hematite | | 3.0 | |
| Hexahydrite | | 2.2 | |
| Hydroxylapatite | 0.2 | 1.4 | |
| Illite | 1.7 | | |
| Jarosite | | | 2.1 |
| Kaolinite | 58.3 | 63.8 | 49.8 |
| Montmorillonite | 1.0 | | 1.4 |
| Pyrite | 0.2 | | 12.3 |
| Quartz | 36.8 | 15.8 | 22.7 |
| Rutile | 0.3 | 0.2 | |
| Siderite | 0.2 | 10.6 | |

The compositions of the laboratory ashes prepared from the feed coals are reported in Table 9.

Table 9. Analyses of Laboratory Ashes of Feed Coals used in Oxy-fuel Tests

| | Acland | Callide | Rolleston |
|------------------------------------|---------------|----------------|------------------|
| % | | | |
| Al₂O₃ | 27.41 | 32.07 | 23.72 |
| CaO | 0.32 | 1.24 | 3.71 |
| Fe₂O₃ | 0.92 | 11.63 | 15.59 |
| K₂O | 0.26 | 0.16 | 0.25 |
| MgO | 0.36 | 0.91 | 2.08 |
| MnO | 0.00 | 0.19 | 0.07 |
| Na₂O | 0.09 | 0.00 | 0.60 |
| P₂O₅ | 0.05 | 0.11 | 1.12 |
| SiO₂ | 67.17 | 50.02 | 48.36 |
| SO₃ | 0.10 | 1.02 | 1.50 |
| TiO₂ | 1.69 | 1.95 | 0.85 |
| Total | 98.4 | 99.3 | 97.9 |

The phase data (XRD) and compositions (majors) of the ashes from the air-fired power stations and the oxy-fuel tests are listed in Table 10 and Table 11, respectively.

Table 10. Inorganic Phases in Ashes from Air-fired and Oxy Fuel Tests.

| | Acland | | Callide | | Rolleston | |
|----------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| | air-fired | oxy-fired | air-fired | oxy-fired | air-fired | oxy-fired |
| Phase (wt %) | | | | | | |
| Quartz | 12.8 | 10.9 | 3.8 | 3.4 | 7.2 | 8.5 |
| Mullite | 29.2 | 32.9 | 32.1 | 32.8 | 17.2 | 22.1 |
| Illite | 0.8 | nd | 1.7 | nd | nd | nd |
| Kaolinite | nd | 0.7 | nd | 1.3 | nd | nd |
| Cristobalite (?) | 0.2 | 0.1 | nd | nd | 0.1 | 0.2 |
| Hematite | nd | nd | 0.2 | 0.0 | 1.0 | 0.7 |
| Maghemite | 1.0 | 1.5 | 0.7 | 1.7 | 1.1 | 0.9 |
| Magnetite | nd | nd | 3.7 | 2.0 | 0.6 | 0.8 |
| Sylvite (KCl) | nd | nd | nd | nd | 0.5 | 1.0 |
| Glass (as tridymite) | 56.0 | 53.8 | 57.8 | 58.9 | 72.4 | 65.9 |

(nd: not detected)

Table 11. Composition of Ashes from Air-fired and Oxy Fuel Tests

| | Acland | | Callide | | Rolleston | |
|------------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
| | air-fired | oxy-fired | air-fired | oxy-fired | air-fired | oxy-fired |
| % | | | | | | |
| C | 0.28 | 0.61 | 0.23 | 0.28 | 0.56 | 0.63 |
| S | 0.20 | 0.17 | 0.16 | 0.13 | 0.56 | 0.60 |
| Al₂O₃ | 29.1 | 30.8 | 35.0 | 35.3 | 26.4 | 27.4 |
| CaO | 0.63 | 0.83 | 1.67 | 1.66 | 2.81 | 2.28 |
| Fe₂O₃ | 2.72 | 4.56 | 11.27 | 11.34 | 11.49 | 9.35 |
| K₂O | 0.55 | 0.41 | 0.44 | 0.45 | 1.49 | 1.71 |
| MgO | 0.46 | 0.61 | 1.13 | 1.12 | 1.72 | 1.47 |
| MnO | 0.04 | 0.08 | 0.19 | 0.18 | 0.06 | 0.07 |
| Na₂O | 0.17 | 0.16 | 0.14 | 0.10 | 0.79 | 0.55 |
| P₂O₅ | 0.16 | 0.18 | 0.25 | 0.29 | 0.96 | 0.78 |
| SiO₂ | 64.1 | 60.9 | 49.5 | 48.8 | 50.6 | 52.5 |
| SO₃ | 0.28 | 0.27 | 0.22 | 0.22 | 1.13 | 1.06 |
| TiO₂ | 1.82 | 1.91 | 2.13 | 2.10 | 1.19 | 1.35 |
| Total | 100.0 | 100.7 | 101.9 | 101.5 | 98.6 | 98.6 |

The concentrations of the trace elements in the ashes are listed in Table 12. Note that F, determined using PIGME and Hg, determined by cold vapour-AFS are included for completeness in this dataset. Note also that As and Se were determined by HGAFS.

Table 12. Concentrations of Trace Elements in Ashes from Air-fired and Oxy Fuel Tests

| | Acland | | Callide | | Rolleston | |
|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| | air-fired | oxy-fired | air-fired | oxy-fired | air-fired | oxy-fired |
| As | 1.4 | 1.8 | 1.6 | 1.7 | 7.6 | 3.7 |
| Bi | 0.48 | 0.47 | 0.34 | 0.37 | 0.48 | 0.37 |
| Cd | 0.34 | 0.26 | 0.22 | 0.26 | 0.26 | 0.26 |
| Co | 66 | 56 | 29 | 34 | 88 | 72 |
| Cr | 91 | 93 | 137 | 148 | 83 | 151 |
| F | 210 | 170 | 120 | 110 | 660 | 630 |
| Hg | 0.077 | 0.061 | 0.086 | 0.058 | 0.197 | 0.269 |
| Mo | 2.7 | 2.6 | 2.1 | 2.1 | 5.3 | 3.6 |
| Ni | 61 | 69 | 118 | 131 | 174 | 175 |
| Pb | 80 | 77 | 84 | 85 | 69 | 63 |
| Sb | 0.79 | 0.66 | 0.32 | 0.35 | 0.87 | 0.68 |
| Se | 1.04 | 1.01 | 0.60 | 0.62 | 1.91 | 1.77 |
| Sn | 8 | 8 | 7 | 7 | 6 | 14 |
| Sr | 0.04 | 0.05 | 0.04 | 0.05 | 0.07 | 0.07 |
| Th | 32 | 24 | <5 | 22 | 21 | 19 |
| Ti | 1.1 | 1.26 | 1.3 | 1.3 | 0.71 | 0.74 |
| U | 13 | 12 | 8 | 9 | 11 | 10 |
| V | 371 | 313 | 178 | 223 | 231 | 228 |
| W | 4 | 5 | 4 | 4 | 10 | 6 |
| Zn | 240 | 190 | 170 | 130 | 220 | 270 |

The pH, conductivity and trace element concentrations of each of the leachates are shown in Tables 13 and 14.

The general observation is that there is little difference between the leach behaviours of ashes obtained from a conventionally fired coal and from the same coal fired in an oxy-fuel boiler. However, there were some differences observed in the analyses of individual leachates for a limited number of specific trace elements from each pair.

Table 13. Analyses of Leachates of Ashes from Air-fired and Oxy Fuel Tests (l:s ratio = 3.5:1).

| | Acland 3.5 | | Callide 3.5 | | Rolleston 3.5 | |
|-----------------------|------------|-----------|-------------|-----------|---------------|-----------|
| | air-fired | oxy-fired | air-fired | oxy-fired | air-fired | oxy-fired |
| pH | 6.4 | 6.1 | 7.5 | 7.5 | 6.5 | 6.2 |
| Condy* | 3.3 | 2.3 | 2.6 | 2.4 | 11.0 | 12.5 |
| mg/L | | | | | | |
| B | 2.61 | 2.19 | 2.89 | 3.00 | 36.8 | 28.7 |
| Ca | 157 | 183 | 192 | 153 | 693 | 708 |
| Fe | nd | nd | nd | nd | nd | nd |
| K | 541 | 274 | 382 | 346 | 2261 | 2668 |
| Mg | 1.3 | 1.2 | 1.5 | 2.0 | 2.5 | 3.0 |
| Na | 28 | 27 | 26 | 22 | 104 | 102 |
| P | 21 | 17 | 9 | 10 | 74 | 79 |
| SO₄ | 787 | 775 | 758 | 664 | 3258 | 3378 |
| Si | 8.3 | 4.0 | 3.2 | 4.8 | 12.4 | 12.4 |
| ug/L | | | | | | |
| Al | 50 | 148 | 77 | 48 | 119 | 382 |
| As | 33 | 9 | 48 | 73 | 27 | 19 |
| Ba | 60 | 56 | 88 | 45 | 48 | 69 |
| Cd | 3.5 | 2.1 | 1.7 | 1.8 | 3.5 | 6.6 |
| Co | 49 | 40 | 3 | 2 | 73 | 100 |
| Cr | 2.7 | 1.4 | 36 | 45 | 16 | 17 |
| Cu | 14 | 4.0 | 9.0 | 6.8 | 10 | 26 |
| Li | 1483 | 1480 | 1903 | 3273 | 3155 | 3852 |
| Mn | 1916 | 2597 | 502 | 502 | 2097 | 4631 |
| Mo | 561 | 245 | 515 | 637 | 581 | 290 |
| Ni | 149 | 129 | 31 | 31 | 279 | 466 |
| Pb | 0.01 | 0.02 | <0.01 | <0.01 | 0.53 | <0.01 |
| Sb | 24 | 12 | 5.3 | 6.8 | 10 | 6.1 |
| Se | 110 | 45 | 72 | 70 | 269 | 344 |
| Sr | 2670 | 4597 | 3216 | 2201 | 7255 | 9202 |
| Th | 0.03 | 0.02 | 0.05 | 0.03 | <0.02 | <0.02 |
| U | 0.05 | 0.02 | 0.22 | 0.14 | 0.01 | 0.03 |
| V | 1286 | 300 | 147 | 326 | 134 | 74 |
| W | 35 | 9 | 26 | 52 | 16 | 6 |
| Zn | 670 | 349 | 48 | 19 | 291 | 1517 |

(* mS/cm nd: not detected)

**Table 14. Analyses of Leachates of Ashes from Air-fired and Oxy Fuel Tests
(l:s = 20:1)**

| | Acland 20 | | Callide 20 | | Rolleston 20 | |
|--------|-----------|-----------|------------|-----------|--------------|-----------|
| | air-fired | oxy-fired | air-fired | oxy-fired | air-fired | oxy-fired |
| pH | 6.48 | 6.39 | 7.34 | 7.68 | 6.78 | 6.32 |
| Condy* | 0.71 | 0.49 | 0.62 | 0.48 | 2.39 | 2.71 |
| mg/L | | | | | | |
| B | 0.58 | 0.46 | 0.75 | 0.56 | 7.28 | 6.83 |
| Ca | 30 | 31 | 37 | 27 | 134 | 136 |
| Fe | -0.08 | -0.03 | -0.08 | -0.08 | -0.08 | -0.08 |
| K | 104 | 52 | 79 | 63 | 400 | 472 |
| Mg | 0.2 | 0.3 | 0.3 | 0.3 | 0.4 | 0.6 |
| Na | 5.2 | 4.9 | 5.2 | 3.8 | 19 | 18 |
| P | 4.2 | 3.2 | 2.2 | 2.0 | 14 | 15 |
| SO4 | 150 | 131 | 150 | 106 | 602 | 616 |
| Si | <1 | <1 | <1 | <1 | 2.5 | 1.8 |
| ug/L | | | | | | |
| Al | 54 | 39 | 104 | 196 | 36 | 119 |
| As | 10 | 7.6 | 33 | 60 | 21 | 14 |
| Ba | 26 | 25 | 28 | 12 | 9.2 | 17 |
| Cd | 0.8 | 0.5 | 0.4 | 0.5 | 0.8 | 1.1 |
| Co | 14 | 5.7 | 0.6 | 0.37 | 13 | 21 |
| Cr | 1.3 | 3.4 | 11 | 13 | 2.4 | 1.8 |
| Cu | 9.3 | 1.1 | 2.6 | 2.1 | 2.6 | 7.5 |
| Li | 278 | 303 | 378 | 453 | 588 | 772 |
| Mn | 611 | 418 | 87 | 47 | 37 | 795 |
| Mo | 92 | 105 | 130 | 162 | 224 | 104 |
| Ni | 44 | 26 | 8 | 5 | 52 | 99 |
| Pb | 0.06 | 0.07 | 0.00 | 0.19 | <0.01 | <0.01 |
| Sb | 6.0 | 5.3 | 2.0 | 2.5 | 4.6 | 2.9 |
| Se | 22 | 12 | 18 | 18 | 59 | 72 |
| Sn | 0.07 | 0.04 | 0.04 | 0.04 | 0.04 | 0.06 |
| Sr | 588 | 796 | 668 | 460 | 1324 | 1813 |
| Th | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.02 |
| U | 0.04 | <0.02 | 0.02 | 0.02 | <0.02 | 0.02 |
| V | 283 | 282 | 96 | 285 | 155 | 56 |
| W | 7.5 | 7.5 | 13 | 25 | 14 | 4.8 |
| Zn | 290 | 47 | 16 | 10 | 46 | 288 |

(* mS/cm)

Investigation of the IGCC Slags

The colour, size and morphologies of the slags obtained from the trials completed at the Siemens facility in Germany are illustrated in the following photographs (Figure 1). It is apparent from these photographs that there is variation in the size distribution and morphology of the gasifier slags. This variation is related to factors such as the fusibility of the coal, the composition of the mineral matter and the temperature of gasification. All other factors being equal, it is likely that variation in the morphology (i.e. particle size and shape, amount of fine material) will have an impact on the leaching characteristics of a particular slag.

Figure 1. Photographs of Gasifier Slags



Test 100



Test 101



Test 102



Test 103



Test 104



Buggenum

The samples were air dried to remove the surface moisture. After air drying, the air dried moisture and ash yield were determined. The loss of mass at the ashing temperature (815°C) provides an indication of the amount of carbon in the slags. Although care has to be applied to the interpretation of the data as the slags (formed in a reducing atmosphere) may well increase in mass during ashing.

The phases (XRD) and the compositions (major elements) of the slags are listed in Tables 15 and 16.

Table 15. Inorganic Phases in Test Slags and Buggenum Slag

| | T100 | T101 | T102 | T103 | T104 | Bugg |
|---------------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Phase (wt %) | | | | | | |
| Anorthite | 5.4 | 0.6 | | | | |
| Calcite | | | 0.2 | 0.2 | | |
| Goethite | 3.2 | 0.2 | | | | |
| Hercynite | 0.5 | | | | | |
| Quartz | 0.1 | 1.1 | 0.8 | 0.1 | | |
| Maghemite | 2.8 | | | | | |
| Magnetite | 2.5 | 0.2 | 0.3 | | | |
| Mullite | | | 0.9 | 0.2 | | |
| Graphite | | | 11.7 | 24.9 | | |
| Amorphous | 85.5 | 97.9 | 86.1 | 74.6 | 100.0 | 100.0 |

Table 16. Compositions of Test Slags and Buggenum Slag

| Test | 100 | 101 | 102 | 103 | 104 | Bugg |
|------------------------------------|------------|------------|------------|------------|------------|-------------|
| % | | | | | | |
| Moist | 0.3 | <0.1 | 0.6 | 0.6 | <0.1 | <0.1 |
| Ash yield | 99.8 | 100.4 | 89.5 | 71.3 | 100.0 | 99.8 |
| C | 1.1 | 1.7 | 11.7 | 21.6 | 0.9 | 1.4 |
| Al₂O₃ | 21.5 | 18.9 | 21.2 | 21.5 | 32.1 | 22.0 |
| CaO | 9.94 | 4.86 | 7.21 | 12.8 | 7.31 | 14.9 |
| Fe₂O₃ | 21.5 | 23.2 | 13.2 | 3.16 | 5.84 | 6.73 |
| K₂O | 0.48 | 0.45 | 0.22 | 0.47 | 0.60 | 0.78 |
| MgO | 2.80 | 2.18 | 0.77 | 0.93 | 2.08 | 1.12 |
| MnO | 0.12 | 0.09 | 0.08 | 0.03 | 0.03 | 0.05 |
| Na₂O | 1.51 | 0.58 | 0.06 | 0.72 | 0.96 | 0.22 |
| P₂O₅ | 0.64 | 0.85 | 1.52 | 1.21 | 0.14 | 0.16 |
| SiO₂ | 41.5 | 48.2 | 41.6 | 34.8 | 51.1 | 54.5 |
| SO₃ | 0.60 | 0.45 | 0.43 | 0.32 | 0.05 | 0.22 |
| TiO₂ | 0.85 | 1.13 | 1.33 | 1.03 | 1.68 | 1.07 |
| LOI | | | 11.7 | 24.9 | | |
| Total | 101.5 | 100.9 | 99.3 | 101.8 | 101.9 | 101.8 |

Table 17. Concentrations of Trace Elements in Slag Samples

| Test | 100 | 101 | 102 | 103 | 104 | Bugg |
|-------------|--------------|------------|------------|------------|------------|-------------|
| | mg/kg | | | | | |
| As | 9.3 | 1.4 | 4.8 | 2.2 | 0.8 | 2.7 |
| B | 200 | 64 | 160 | 40 | 91 | 120 |
| Ba | 2900 | 3600 | 2200 | 480 | 1300 | 840 |
| Be | 9 | 17 | 5 | 3 | 6 | 9 |
| Bi | 0.79 | nd | nd | nd | nd | nd |
| Cd | 0.2 | nd | 0.18 | 0.16 | nd | nd |
| Cl | 300 | 40 | 65 | 68 | nd | 73 |
| Co | 61 | 100 | 41 | 56 | 38 | 51 |
| Cr | 1000 | 780 | 200 | 190 | 200 | 93 |
| Cu | 100 | 71 | 91 | 53 | 56 | 29 |
| F | 200 | 90 | 220 | 380 | 90 | 60 |
| Hg | 0.09 | 0.02 | 0.23 | 0.3 | nd | nd |
| Li | 64 | 29 | 35 | 150 | 67 | 62 |
| Mn | 890 | 660 | 590 | 150 | 260 | 390 |
| Mo | 200 | 27 | 14 | 6 | 14 | 4 |
| Nb | 35 | 47 | 17 | 10 | 15 | 16 |
| Ni | 240 | 240 | 320 | 98 | 79 | 76 |
| Pb | 35 | 8 | 12 | 17 | 4 | nd |
| Sb | 1.9 | 0.4 | 0.5 | 0.6 | nd | 0.2 |
| Sc | 15 | 18 | 25 | 18 | 32 | 26 |
| Se | 1.7 | 0.5 | 0.9 | 0.9 | 0.2 | nd |
| Sn | 34 | 12 | 38 | 27 | 8 | nd |
| Sr | 2400 | 2200 | 1400 | 390 | 1400 | 530 |
| Th | 28 | 40 | 15 | 13 | 17 | 17 |
| U | 9 | 11 | 4 | 5 | 6 | 6 |
| V | 150 | 140 | 110 | 87 | 240 | 170 |
| W | 17 | 13 | 5 | 4 | 4 | 5 |
| Y | 82 | 120 | 67 | 44 | 63 | 73 |
| Zn | 180 | 75 | 62 | 130 | 17 | 10 |

(nd: not detected)

Table 18. Analyses of Leachates of Slag Samples (l:s = 3.5:1)

| | T100-35 | T101-35 | T102-35 | T103-35 | T104-35 | BUG-35 |
|-----------------------|---------|---------|---------|---------|---------|--------|
| pH | 7.46 | 7.85 | 7.82 | 9.09 | 8.68 | 8.05 |
| Condy* | 0.53 | 0.16 | 0.60 | 0.79 | 0.08 | 0.21 |
| mg/L | | | | | | |
| B | 0.33 | 0.06 | 0.14 | 0.06 | 0.01 | 0.09 |
| Ca | 81 | 22 | 104 | 142 | 8 | 28 |
| Fe | 0.16 | 0.05 | 0.02 | 0.07 | 0.30 | 0.15 |
| K | 1.73 | 0.62 | 1.86 | 2.31 | 0.30 | 0.61 |
| Mg | 8.51 | 2.58 | 4.65 | 2.11 | 0.85 | 0.58 |
| Na | 7.53 | 4.53 | 5.56 | 16.47 | 5.63 | 9.19 |
| P | 0.00 | 0.04 | 0.77 | 0.55 | 0.39 | 0.40 |
| SO₄ | 201 | 46 | 255 | 435 | 18 | 52 |
| Si | 2.38 | 0.71 | 1.18 | 0.18 | 1.59 | 1.46 |
| µg/L | | | | | | |
| Al | 129 | 958 | 552 | 5864 | 1924 | 126 |
| As | 0.48 | 1.78 | 8.02 | 3.47 | 8.90 | 1.06 |
| Ba | 104 | 169 | 350 | 68 | 53 | 4 |
| Cd | 2.96 | 2.80 | 3.04 | 3.14 | 3.00 | 2.75 |
| Co | 1.33 | 0.64 | 1.27 | 1.48 | 0.41 | 2.08 |
| Cr | 1.03 | 0.90 | 0.87 | 1.00 | 1.75 | 0.80 |
| Cu | 1.44 | 1.13 | 0.81 | 1.80 | 2.42 | 0.90 |
| Li | 57 | 31 | 42 | 85 | 9 | 15 |
| Mn | 240 | 12 | 29 | 0.39 | 8 | 0.24 |
| Mo | 198 | 76 | 79 | 239 | 19 | 49 |
| Ni | 30 | 10 | 21 | 1 | 14 | 11 |
| Pb | 0.15 | 0.21 | 0.12 | 0.12 | 1.42 | 0.16 |
| Sb | 1.40 | 3.62 | 3.55 | 10.29 | 1.39 | 1.41 |
| Se | 11 | 6 | 57 | 15 | 22 | 9 |
| Sr | 2962 | 872 | 2074 | 522 | 271 | 74 |
| Th | 0.02 | 0.00 | 0.05 | 0.03 | 0.08 | 0.00 |
| U | 0.30 | 0.75 | 0.74 | 0.13 | 0.11 | 0.18 |
| V | -0.52 | 0.54 | 0.56 | 5.17 | 7.49 | -0.39 |
| W | 0.44 | 2.40 | 1.74 | 8.45 | 0.64 | 1.87 |
| Zn | 11.6 | 5.9 | 9.1 | 8.8 | 9.2 | 2.9 |

(* mS/cm)

Table 19. Analyses of Leachates of Slag Samples (l:s = 20:1)

| | T100-20 | T101-20 | T102-20 | T103-20 | T104-20 | BUG-20 |
|-----------------------|---------|---------|---------|---------|---------|--------|
| pH | 7.33 | 7.72 | 7.94 | 9.83 | 8.64 | 7.99 |
| Condy* | 0.11 | 0.06 | 0.16 | 0.24 | 0.02 | 0.04 |
| mg/L | | | | | | |
| B | <0.04 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Ca | 16.2 | 9.6 | 24.0 | 39.7 | 1.9 | 5.3 |
| Fe | 0.05 | 0.04 | 0.02 | 0.02 | 0.06 | 0.42 |
| K | 0.50 | 0.37 | 0.65 | 0.70 | 0.25 | 0.38 |
| Mg | 1.15 | 0.80 | 0.89 | 0.63 | 0.15 | 0.12 |
| Na | 1.36 | 1.43 | 1.33 | 3.38 | 1.21 | 1.59 |
| P | 0.00 | 0.14 | 0.68 | 0.21 | 0.00 | 0.03 |
| SO₄ | 24 | 12 | 46 | 85 | 0.9 | 8.4 |
| Si | 0.91 | 0.72 | 0.86 | 1.16 | 0.18 | 0.44 |
| ug/L | | | | | | |
| Al | 337 | 1029 | 1428 | 3843 | 279 | 162 |
| As | 0.22 | 1.55 | 24.8 | 4.65 | 0.79 | 0.71 |
| Ba | 65 | 112 | 171 | 23 | 10 | 2.1 |
| Cd | 2.80 | 2.78 | 2.99 | 2.67 | 2.69 | 2.74 |
| Co | 0.25 | 0.21 | 0.20 | 0.36 | 0.26 | 1.37 |
| Cr | 0.64 | 0.71 | 0.67 | 0.64 | 0.53 | 0.61 |
| Cu | 0.92 | 1.01 | 1.85 | 1.39 | 1.60 | 1.73 |
| Li | 9.51 | 6.93 | 9.52 | 18.61 | 1.24 | 2.40 |
| Mn | 24 | 9.9 | 4.9 | 0.1 | 17 | 0.5 |
| Mo | 49.83 | 14.31 | 17.34 | 37.82 | 1.58 | 6.00 |
| Ni | 4.93 | 2.51 | 3.51 | 0.46 | 11.47 | 8.40 |
| Pb | 0.22 | 0.30 | 0.22 | 0.29 | 0.65 | 0.15 |
| Sb | 0.50 | 0.70 | 1.20 | 4.17 | 0.20 | 0.31 |
| Se | 2.8 | 2.4 | 37 | 11 | 1.2 | 2.2 |
| Sr | 783 | 362 | 594 | 134 | 28 | 16 |
| Th | 0.02 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 |
| U | 0.03 | 0.07 | 0.05 | 0.04 | 0.01 | 0.00 |
| V | -0.73 | 0.85 | 2.17 | 8.43 | -0.21 | -0.45 |
| W | 0.43 | 0.63 | 0.85 | 2.95 | 0.23 | 0.78 |
| Zn | 3.4 | 5.5 | 4.0 | 8.1 | 12 | 4.5 |

(* mS/cm)

DISCUSSION

FBC Ashes

The mineralogy of the FBC ashes (both fly ash or silo ash and bottom ash) is characterised by the abundance of calcium-rich phases e.g. calcite and anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$ (Table 4). This is particularly so in the ash from Karita. The high calcium is also evident in the data on the chemical composition (Table 5). Although lower proportions of Ca are found in the ashes from the Australian station, compared with the ash from Karita, the Ca concentrations are still higher than seen in ashes from Australian bituminous coals. Also high are the pH levels of the leachates derived from these materials. Of the trace elements in the samples and also in the leachates, Ba and Sr are particularly high (Tables 6 & 7).

The presence of high levels of Ca, Ba and Sr, arising as a consequence of the addition of limestone to the bed material in FBC systems, is the major difference between ash materials from FBC systems and from conventional coal-fired power stations. Obviously there is a greater mass of waste ash from FBC systems because limestone is added to the bed.

It is not evident from the data in Tables 6 and 7 that ashes from FBC are “better environmentally” than ashes from conventional pf-fired power stations. However, the greater concentrations of Ca and of the associated mineral phases indicate that FBC ashes would have greater neutralisation capacity, and therefore would be suited for backfilling at mine sites where acid mine drainage (AMD) may be a problem. Of interest is the very low concentration (below detection limit) of Mg in the leachates of the ash products from the Karita FBC plant. Presumably this is a consequence of the presence of carbonate and the subsequent formation of insoluble magnesium carbonate.

The leachate data from Table 7 are plotted as histograms in Appendix 1.

Ashes from Oxy Fuel Systems

The ashes produced in the oxy-fuel tests are very similar to the ashes from the same coals used in conventional pf power stations. The mineral phases in the three coals used are given in Table 8. There is nothing remarkable about these data. One comment that can be made is that the mineral phases in the three coals differ significantly. However, the inorganic phases in the paired ashes are almost identical (Table 10). The exception to this is the higher glass content in the ash from the air-firing of the Rolleston coal and thus the lower concentrations of quartz and mullite. There is a similar but less marked variation in the ashes from the Acland coal. As expected, the elemental compositions of each of the paired ashes are similar (Table 11), with two significant differences. The concentrations of Fe and Si vary in the ashes of the Acland and Rolleston pairs. This may in part be the explanation for the variation in the inorganic phases seen within the ash pairs. The presence of sylvite (KCl) in the ashes from the Rolleston coal is intriguing and is likely related to the higher chloride and lower mineral matter in the feed coal.

The concentrations of the trace elements in each of the paired ashes are also remarkably similar (Table 12), with one significant exception. Cr in the oxy-fuel fired ash from the Rolleston coal is higher than in the air-fired ash. There is no obvious explanation. The concentrations of trace elements in the leachates are also generally similar in the ashes from each pair (Tables 13 & 14). However, there is a much higher concentration of Zn in the leachates (both at 3.5:1 and 20:1) of the ash from the oxy-fuel fired Rolleston coal. Again, there is no obvious reason for this.

There are some other exceptions to the general observation that there are no differences in the concentration and leachability of the trace elements in each of the paired ashes. Most trace elements, including the environmentally important ones such as Cd and Se, are leached in similar concentrations. However the leachabilities of some trace elements within pairs did differ, e.g. Mn and Cu. The leachate data are plotted in histograms in Appendix 2.

IGCC Slags

It is apparent from the photographs (Fig. 1) of the IGCC slags from the tests in Germany that there is variation in the size distribution and morphology of these slags. This variation is related to factors such as the fusibility of the coal ash, the composition of the mineral matter and the temperature of gasification. All other factors being equal, it is likely, that variation in the morphology (i.e. particle size and shape) will have an impact on the leaching characteristics of a particular slag.

The variations in the inorganic phases (Table 15) in the slags are interesting, and provide some evidence for the propensity of each of the coals to produce slags under the conditions of the firing. For example, the slags from Test 105 and from Buggenum are completely amorphous. The presence of discrete mineral phases rather than an amorphous phase is indicative of poor melting and subsequently poor slagging. Note also that the slags from Tests 102 and 103 contain high concentrations of “graphite”, which is obviously an indication of poor gasification. This is further reflected in the C content of these slags and their high LOI values (Table 16).

Generally, the compositions of the slags, when expressed as oxides, appear to be similar to those of the respective coal ashes. This is possibly a result of expressing the compositions determined by XRF in the traditional manner, as it is expected that more reduced species of some the major elements would in fact be present e.g. FeO rather than Fe₂O₃. The trace element concentrations in the slags are similar to those reported in the coal ashes (Table 17). However Cr is markedly higher in the slags from Tests 100 and 101. It is obvious, however, from the leach data in Tables 18 and 19 that the Cr in these two samples is not readily leached. The leachate data are plotted in histograms in Appendix 3.

The overall leachability (or solubility) of elements from the slags is lower than that for typical ashes from conventional pf-fired power stations or from the FBC or oxy-fuel fired systems in the present test program. This is evident from a comparison of the conductivities of the leachates (Tables 7, 13, 14, 18 & 19); the conductivities of leachates (l:s = 20:1) from the FBC ashes range from 1.38 to 8.24 mS/cm; the conductivities of the ashes from the conventional pf and oxy-fuel tests range from 0.48 to 2.71 mS/cm whereas the conductivities of the leachates from the IGCC slags range from 0.02 to 0.24 mS/cm. However some trace elements appear from the study to be leached at similar concentrations to those leached from conventional coal pf-fired power station ashes.

CONCLUDING REMARKS

The aim of this report was a comparison of the leachability of trace elements from the fly ash of conventional coal-fired power stations and major waste streams (ash or slags) of transitional technologies such FBC, coal-fired oxy-fuel stations and IGCC systems.

The data has been discussed in the preceding section. However in conclusion, it is worth summarising the findings and tabulating the leachability of a number of the “environmentally significant” trace elements. In an earlier report to the CCSD, Riley (2007) quoted results for trace elements in leachates (l:s ratios of 20:1) of fly ashes from conventional pf-fired power stations in Australia. In Table 20, the ranges are listed and compared with the ranges of a number of trace elements of the ashes or slags (from the transitional technologies) studied in this work.

Table 20. Comparison of Leachates from Ash/Slag from Conventional and Transitional Technologies

| | Leachates (20:1) of ash or slags from | | | |
|-------------|--|-------------|-----------------|-------------|
| | Conventional pf # | FBC | Oxy-fuel | IGCC |
| pH | 4.4 - 12.0 | 8.6 – 12.3 | 6.3 - 7.7 | 7.3 - 9.8 |
| ug/L | | | | |
| As | <2 - 20 | 0.3 - 2.1 | 7 - 60 | 0.2 - 25 |
| B | 60 - 945 | <200 - 800 | 460 - 7280 | <10 - 40 |
| Be | <0.2 - 16 | na | na | na |
| Cd | <0.2 - 5.5 | 0.05 - 0.13 | 0.4 - 1.1 | 2.8 - 3.0 |
| Co | <0.2 - 145 | 0.6 - 1.2 | 0.6 - 21 | 0.2 - 1.4 |
| Cr | <1 - 48 | 1.8 - 37 | 1.3 - 13 | 0.5 - 0.7 |
| Cu | <1 - 275 | 0.2 - 1.4 | 1 - 9.3 | 0.9 - 1.9 |
| Mn | <0.2 - 365 | <0.2 - 2118 | 37 - 795 | 0.1 - 24 |
| Mo | 5 - 275 | 22 – 52 | 92 - 224 | 1.5 - 50 |
| Ni | 1 - 193 | 0.4 – 3 | "5 - 99 | 0.5 - 12 |
| Pb | <0.2 - 1.9 | <0.2 - 8 | <0.2 - 0.2 | <0.2 - 0.7 |
| Sb | <0.1 - 9 | <0.1 - 2 | 2.0 - 6.0 | 0.2 - 4.2 |
| Se | "3 - 60 | 1 – 37 | 12 - 72 | 1 - 37 |
| V | 5.6 - 70 | <5 - 125 | 56 - 285 | <5 - 9 |
| Zn | < 1 - 1900 | "8 – 11 | 10 - 290 | "3 - 12 |

(# data extracted from Riley (2007); na: not available;)

It is apparent from the summary data that generally

- most trace elements leach from the fly ash and bottom ash of FBC systems at similar concentrations to those present in the leachate of ash from conventional power stations (i.e. using coal fired as pulverised fuel in air), although there are possibly some exceptions. Lower concentrations of Cd, Co, Ni and Zn were found in the leachates of the ash from the Australian and Karita FBC power stations.
- trace elements leach similarly from fly ash from coal fired in conventional and oxy-fuel combustion conditions; indeed there does not appear to be any significant differences in the leach behaviour of trace elements in the ashes from the different systems.
- some of the trace elements in the gasifier slags do not leach as readily as those in the fly ash from conventional power stations; these trace elements are B, Cr, Mn, V and Zn and possibly Co and Cu. However, there does not appear to be any change in the leachability of the other trace elements including As and Se. Certainly, IGCC slag obviously has a larger particle size and is less soluble than ash. Although it is sometimes claimed that slag from IGCC plants “is environmentally benign and can be safely landfilled”, obviously care must be taken with its disposal as there are trace elements that can be leached.

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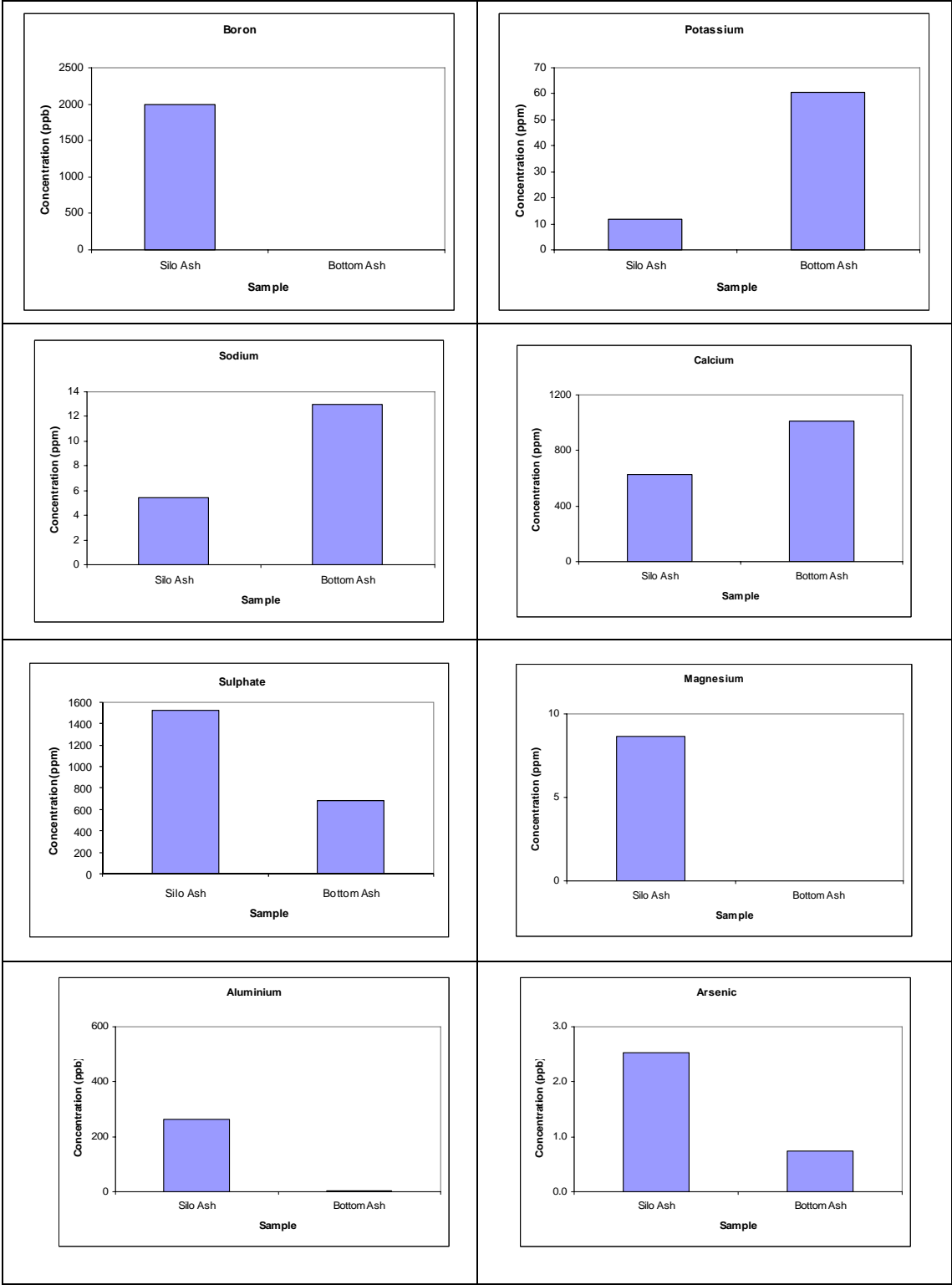
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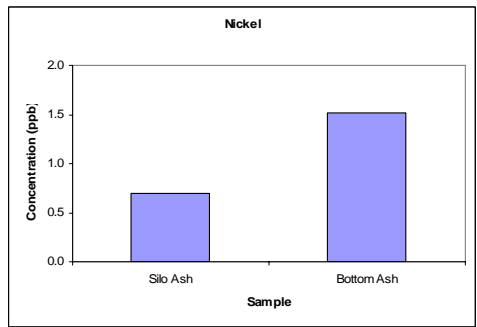
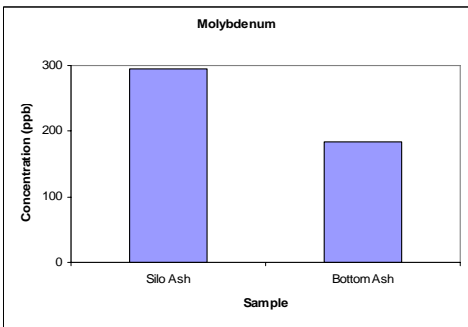
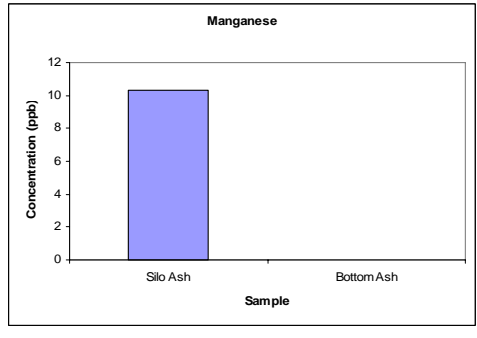
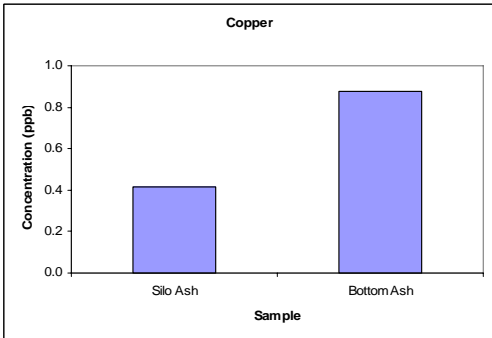
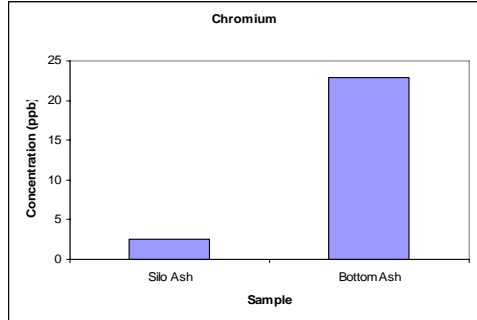
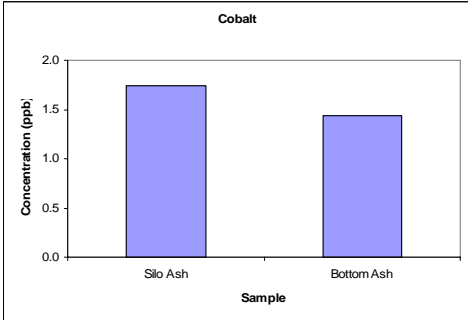
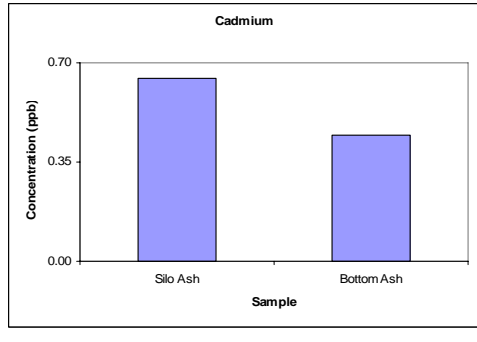
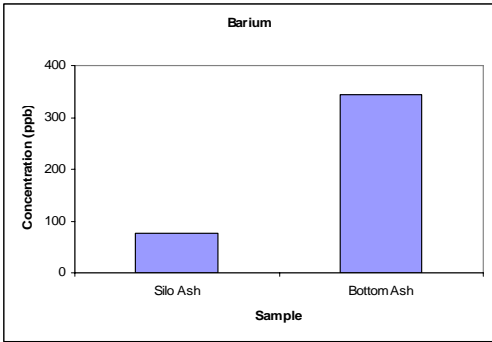
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APPENDIX 1. COMPARISON OF THE LEACH DATA ON THE ASHES FROM THE FBC PLANTS

Table A1.1 Histograms of Data from Leaching of the Australian Ashes (at l:s ratio of 3.5:1)





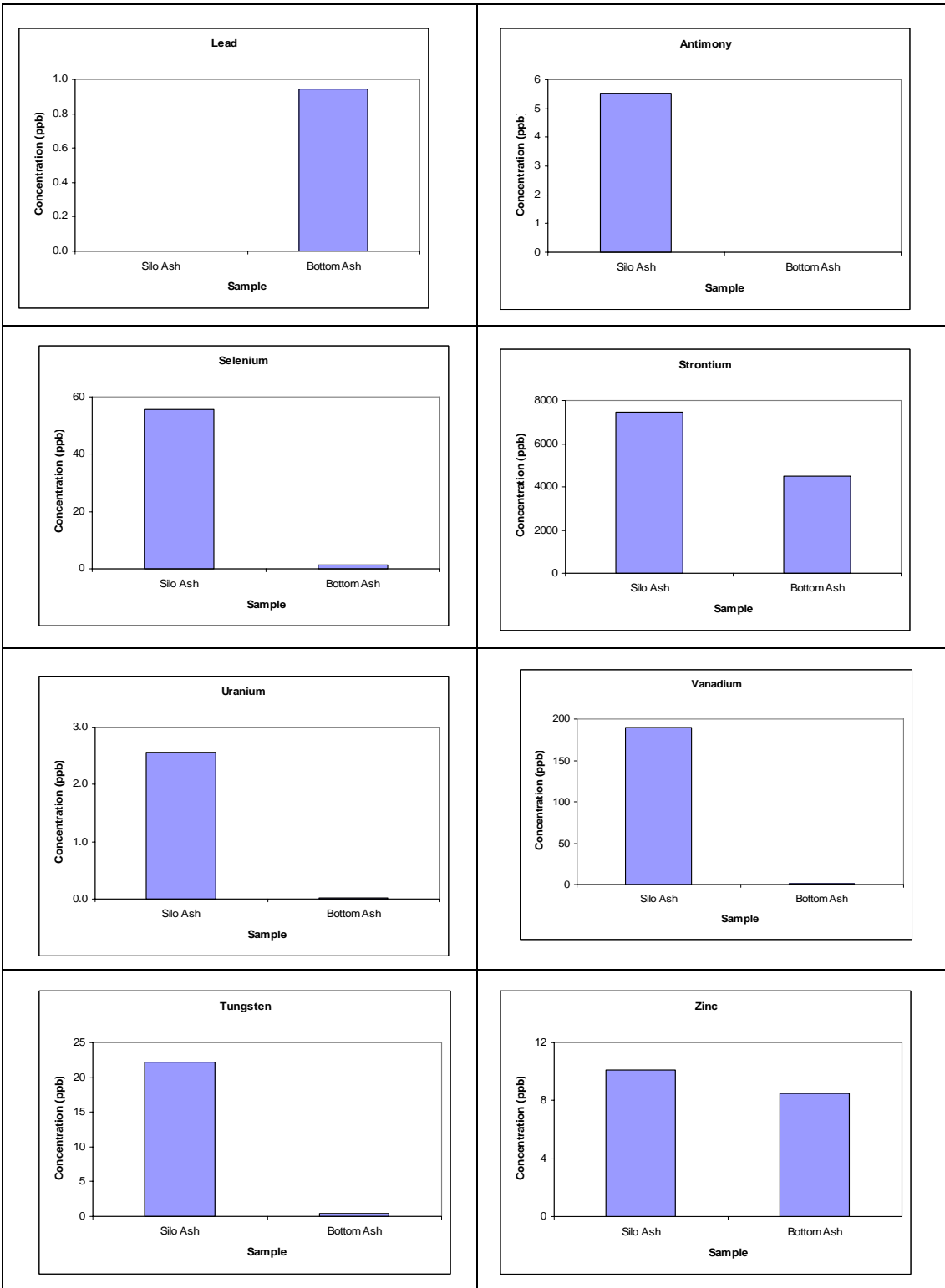
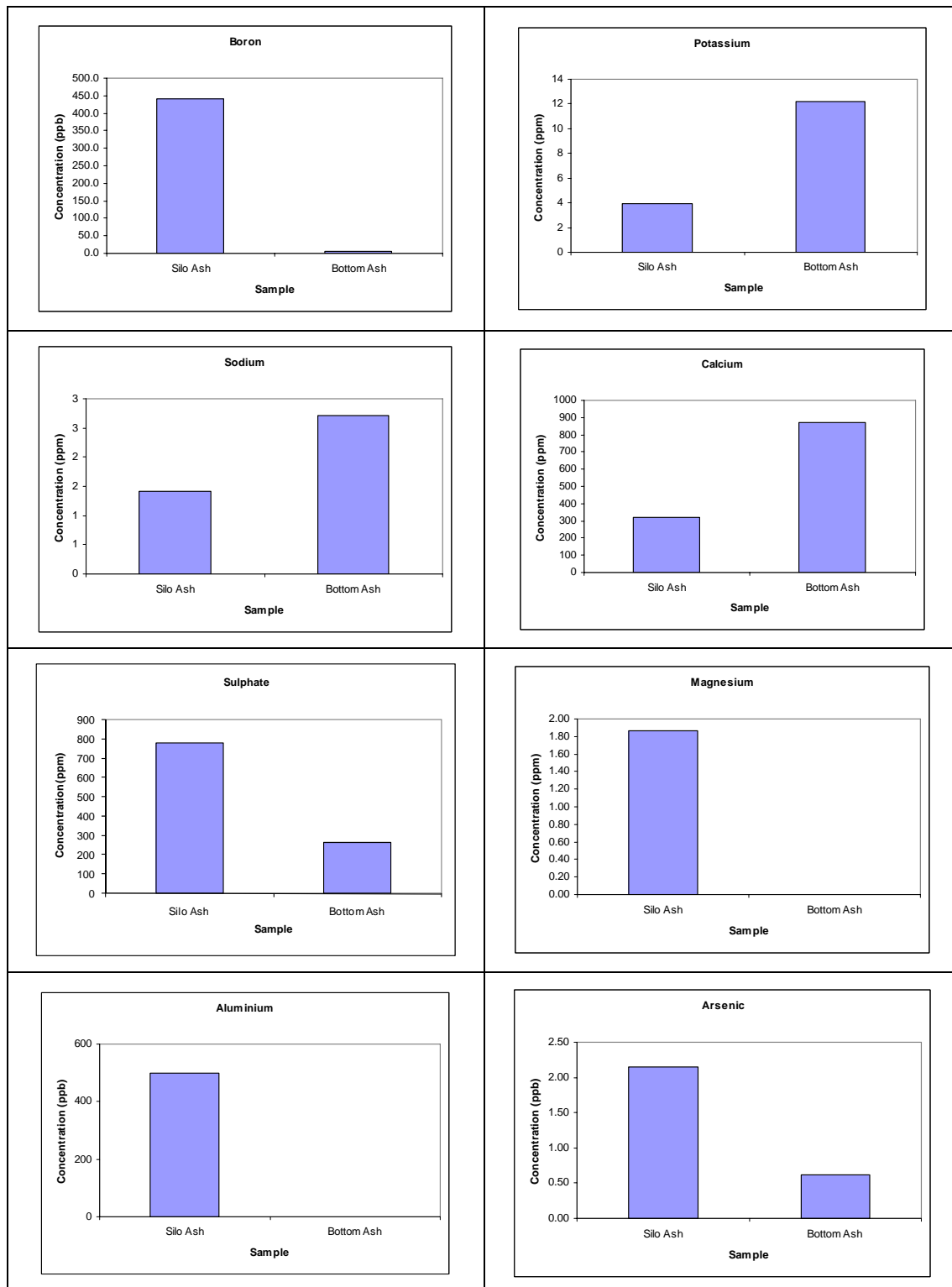
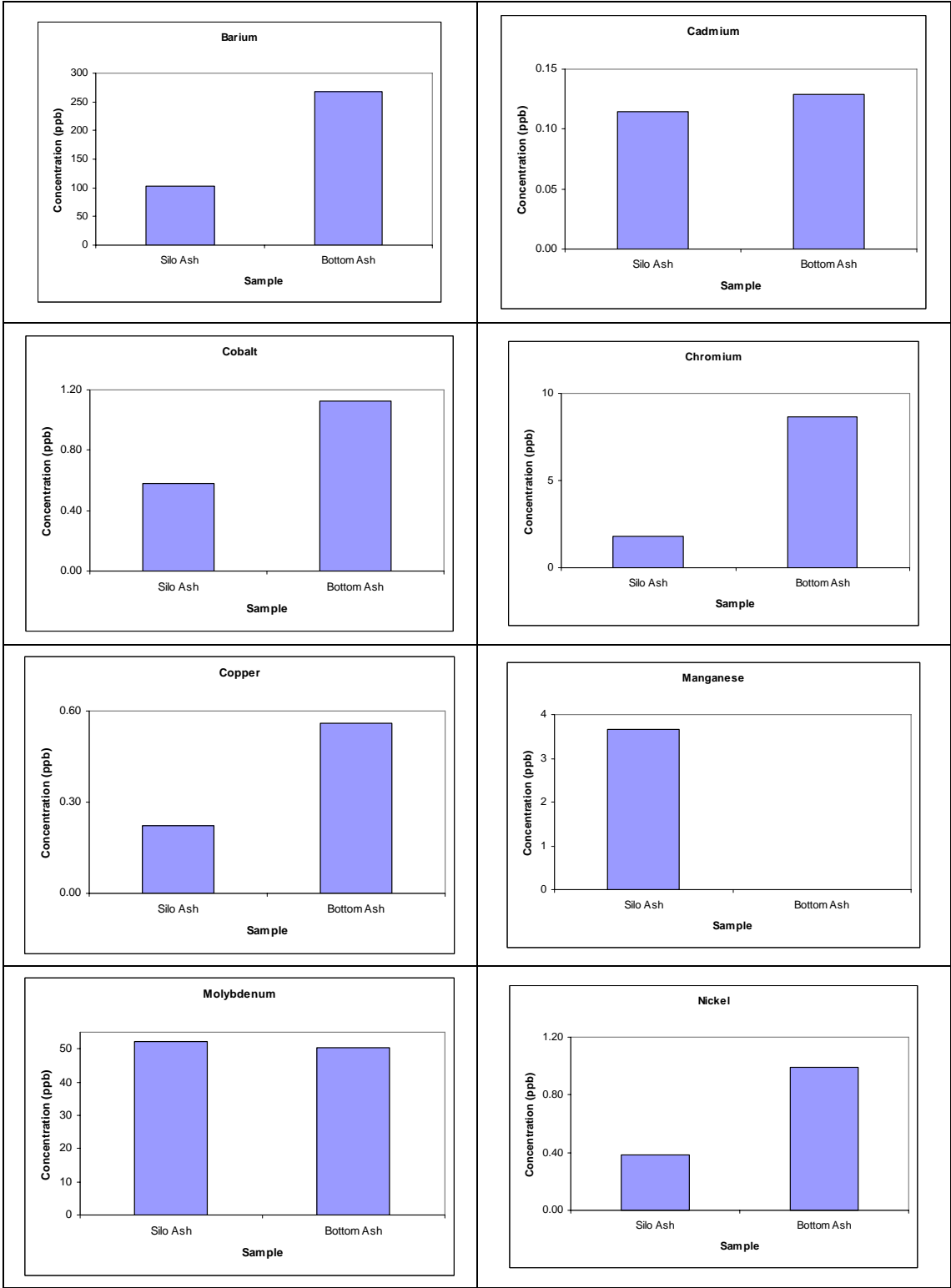


Table A1.2 Histograms of Data from Leaching of the Australian Ashes (at 1:s ratio of 20:1)





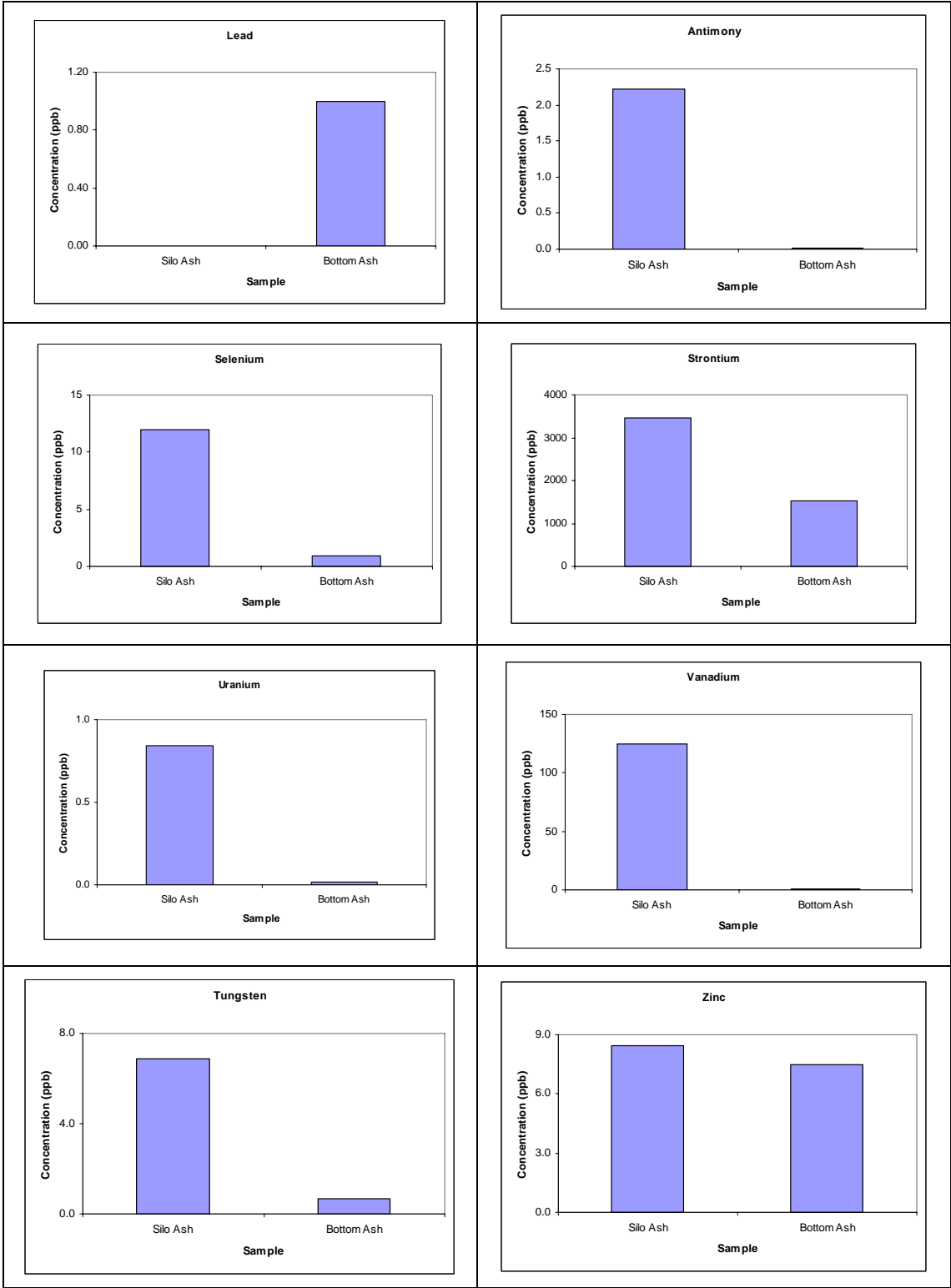
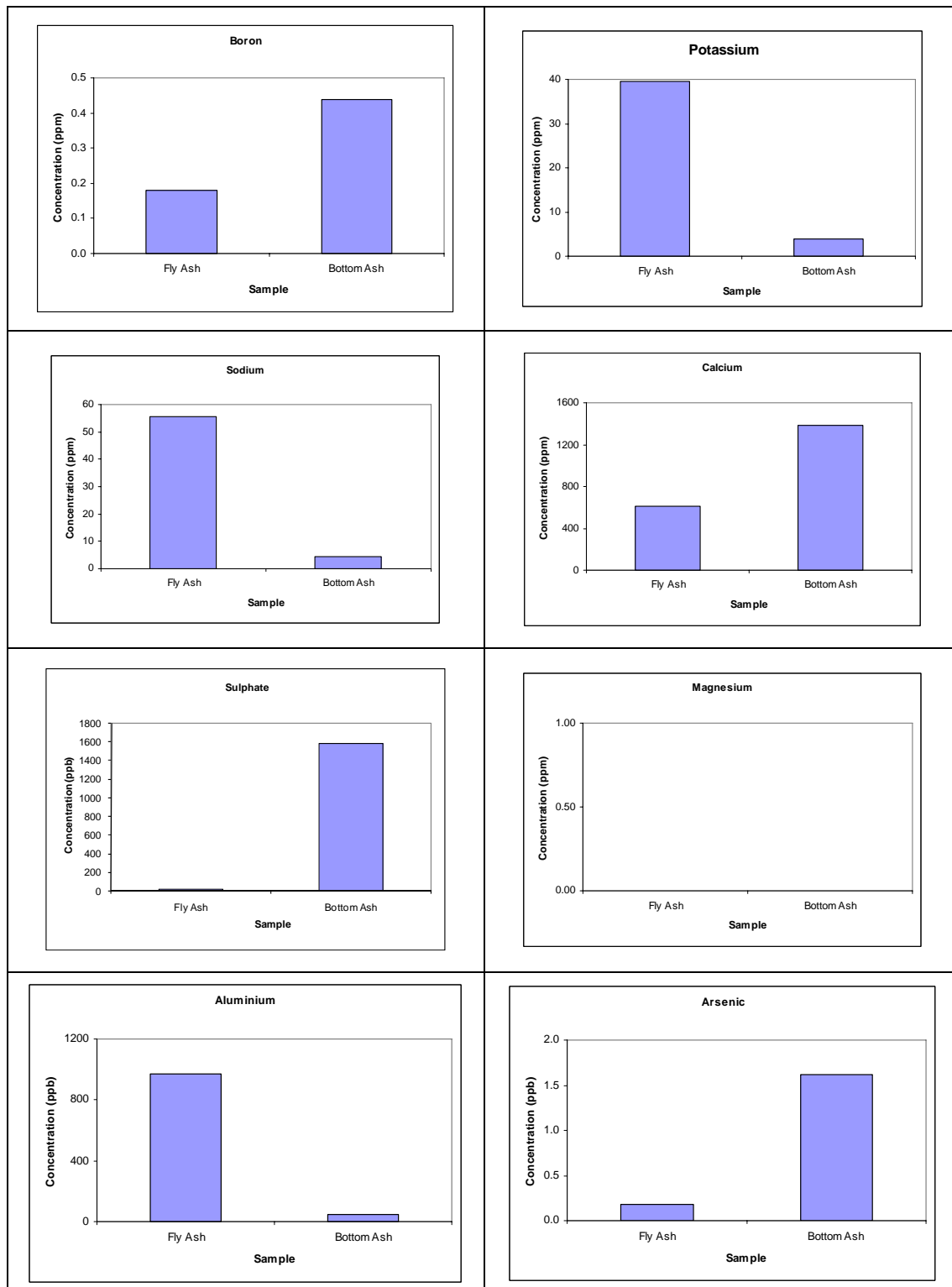
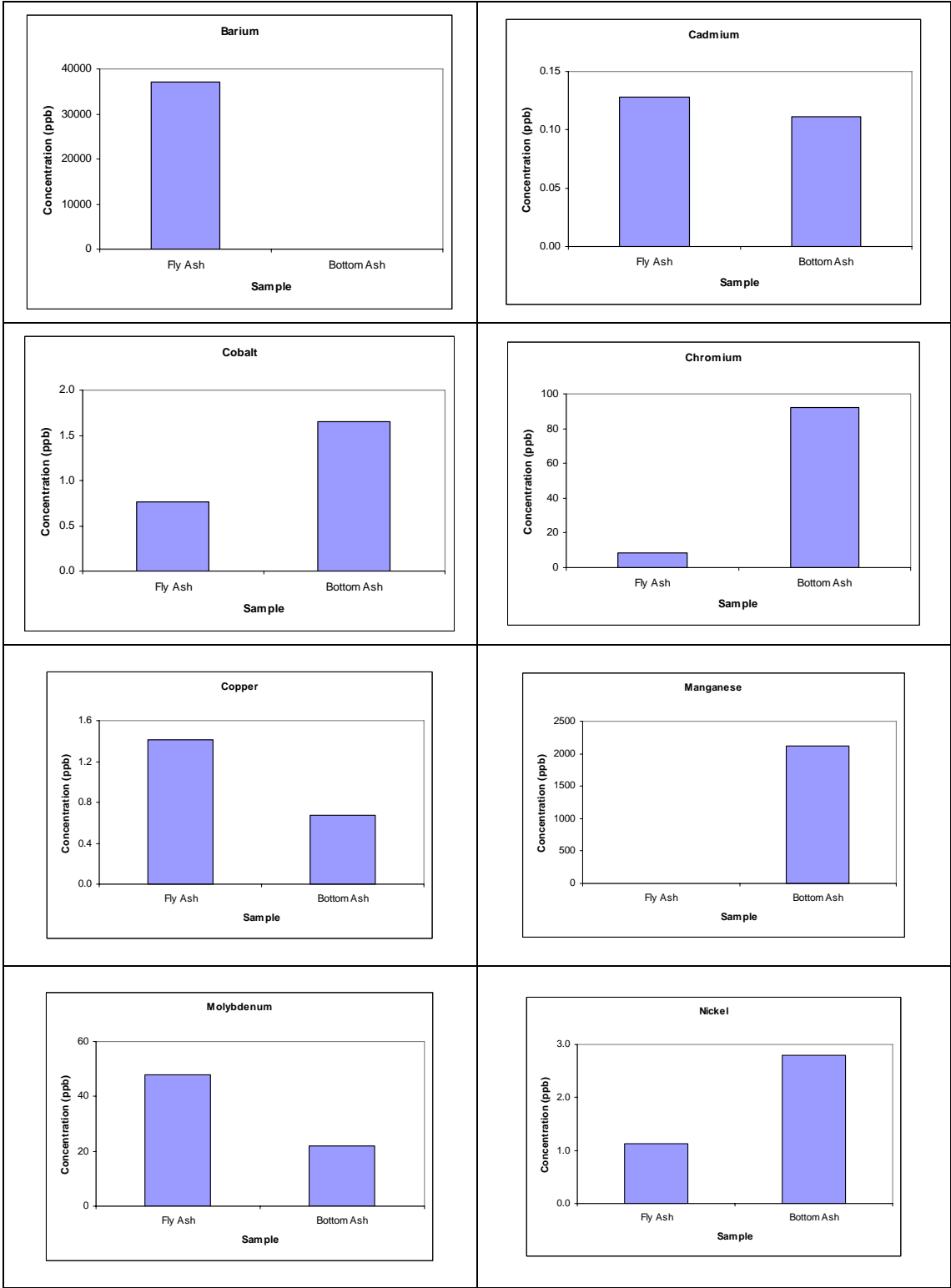


Table A1.3 Histograms of Data from Leaching of Karita Ashes (l:s ratio = 3.5:1)





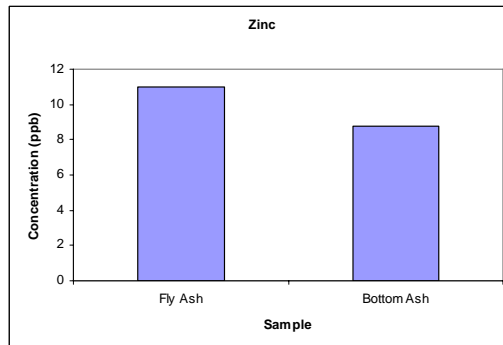
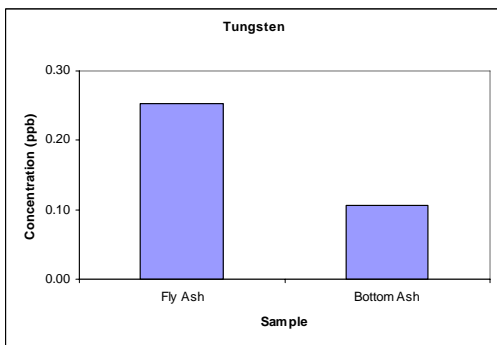
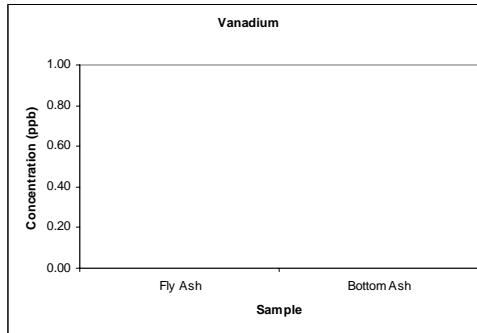
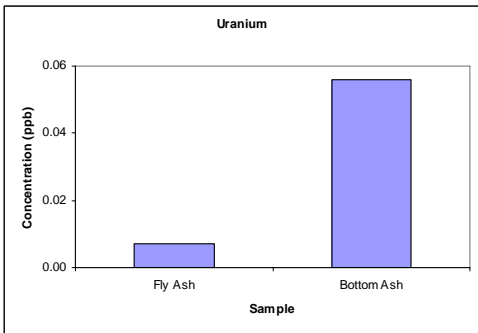
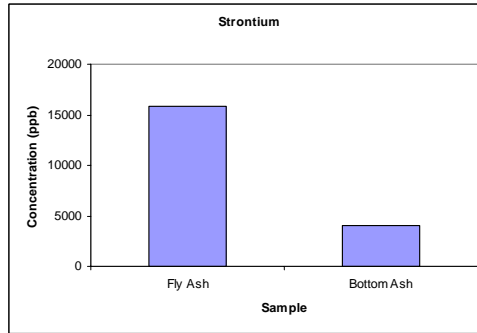
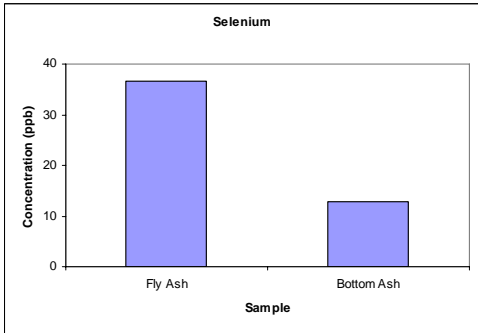
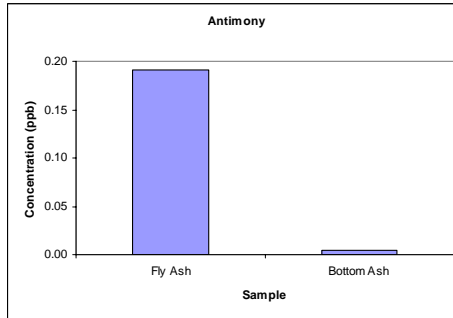
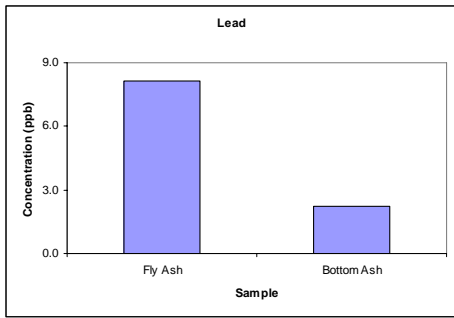
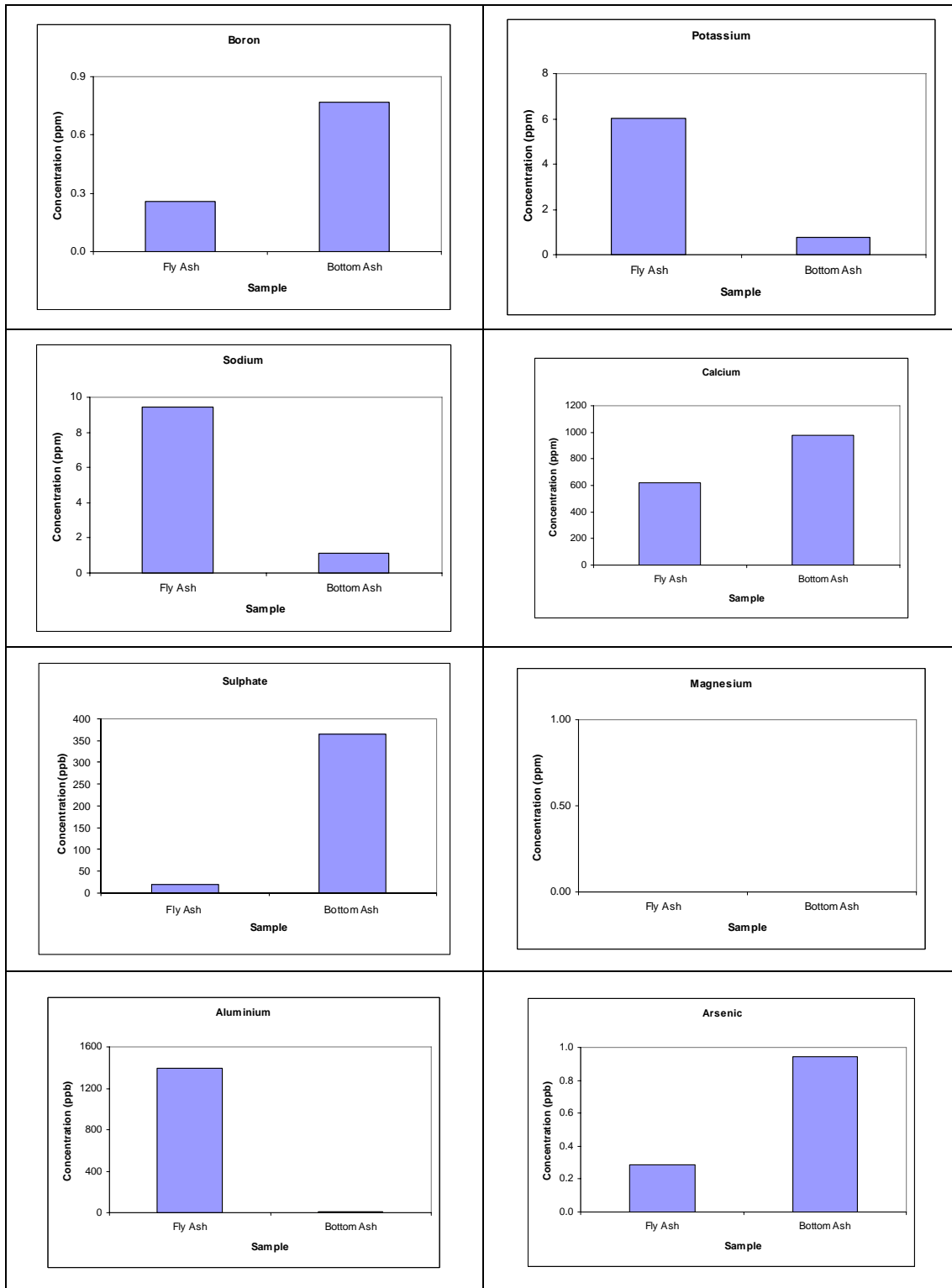
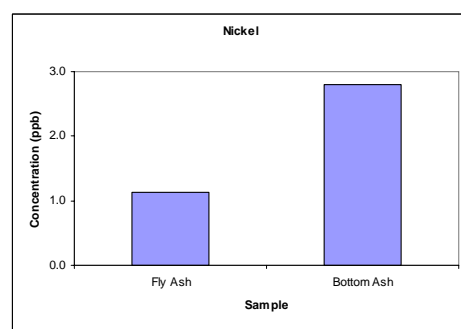
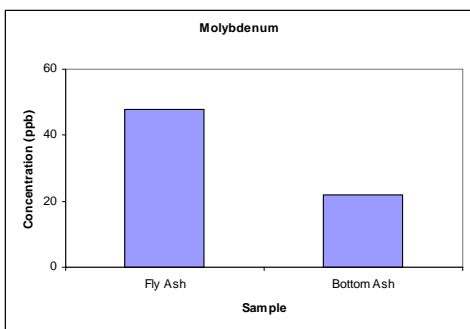
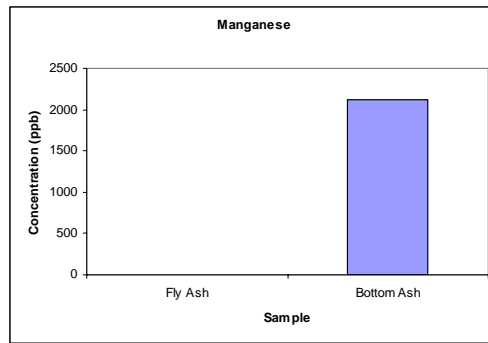
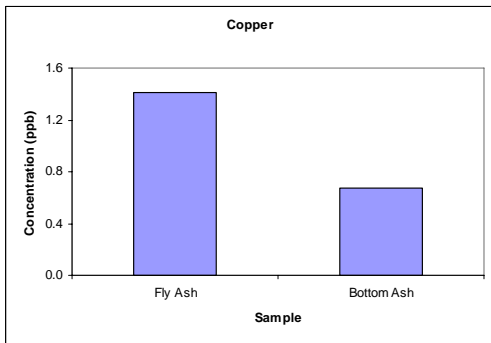
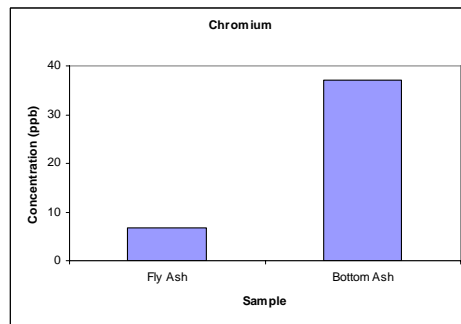
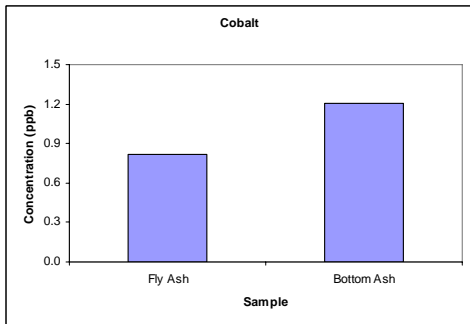
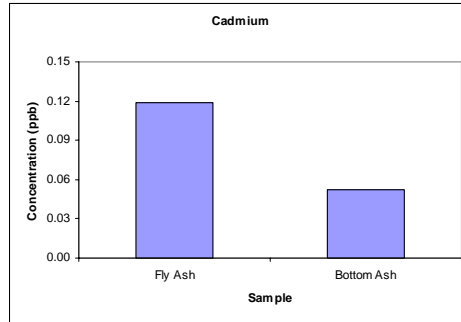
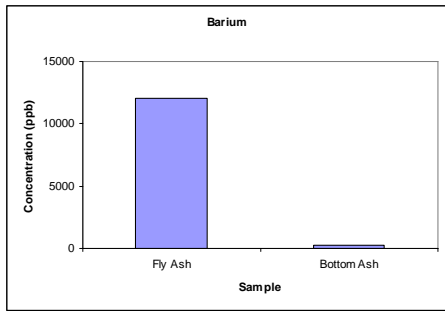
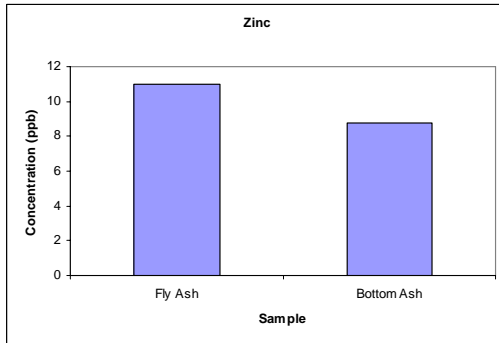
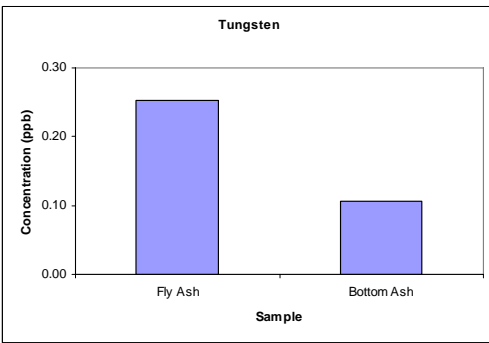
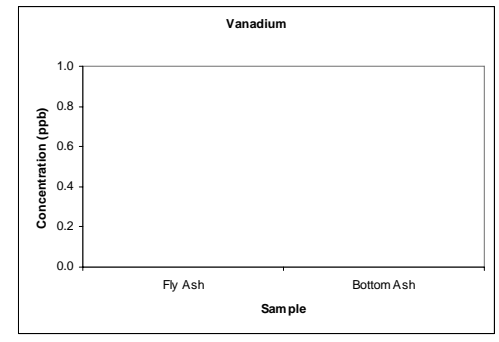
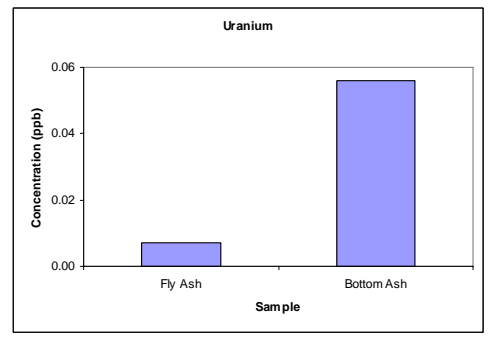
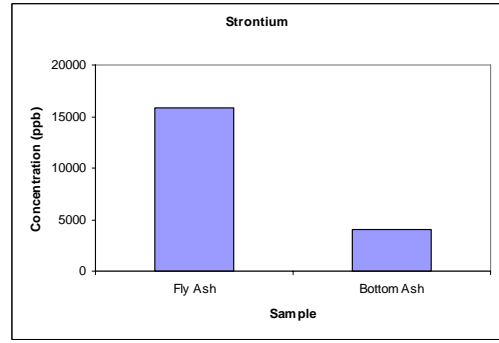
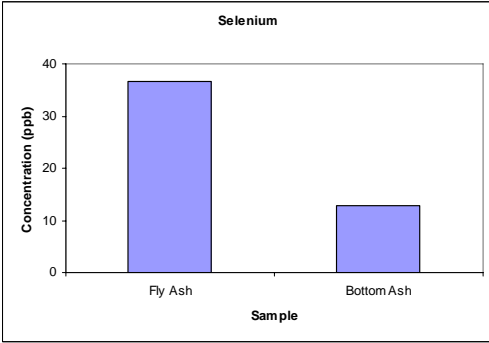
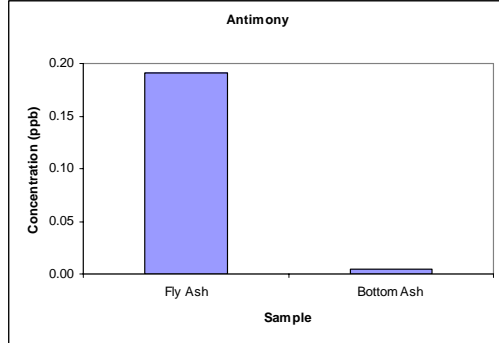
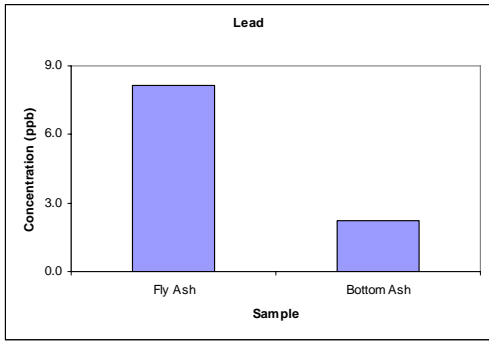


Table A1.4 Histograms of Data from Leaching of Karita Ashes (l:s ratio of 20:1)

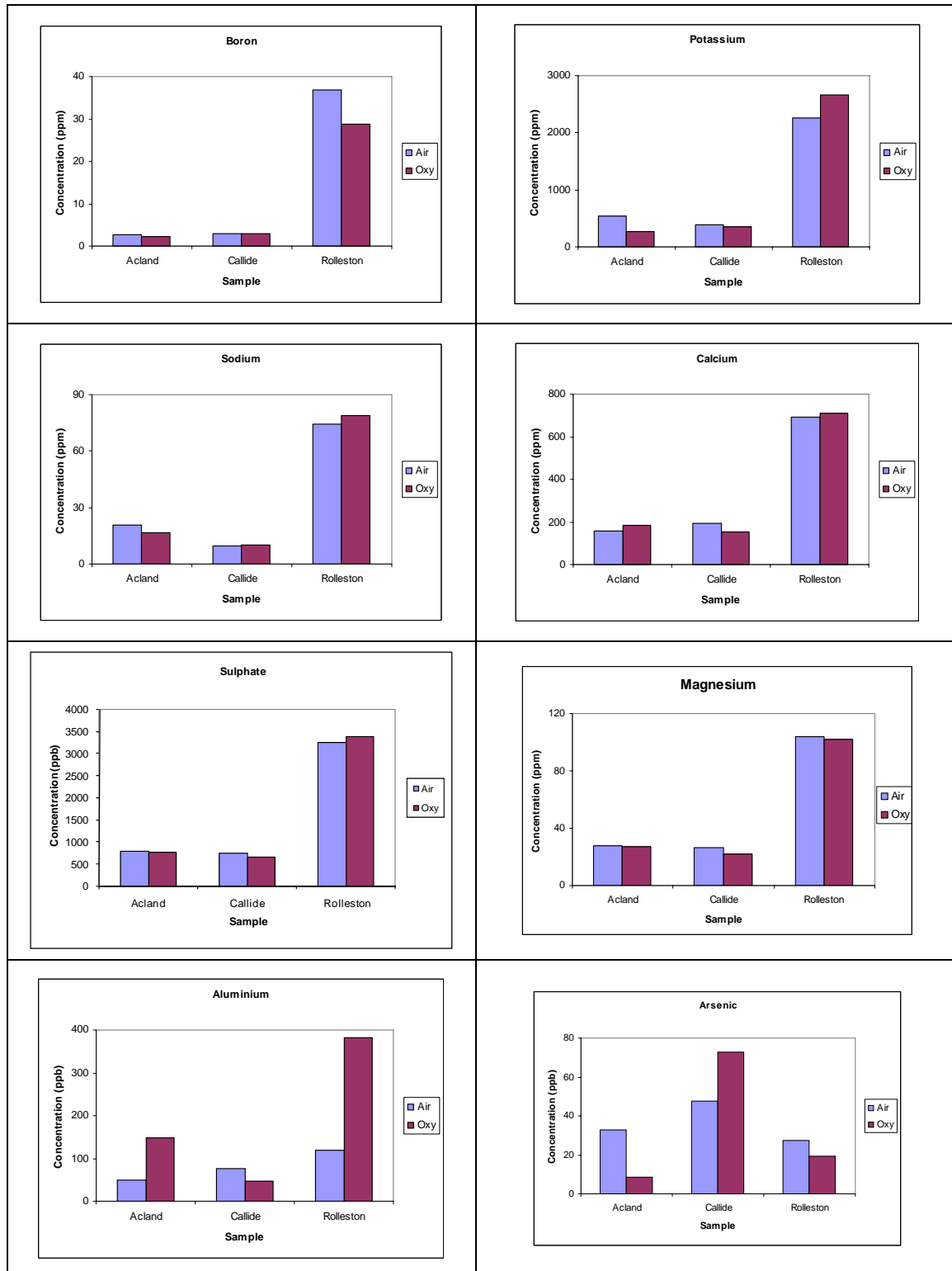


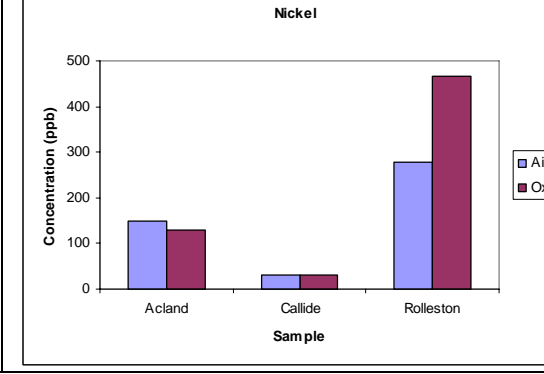
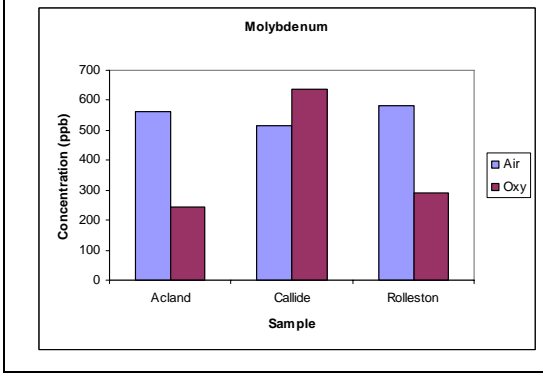
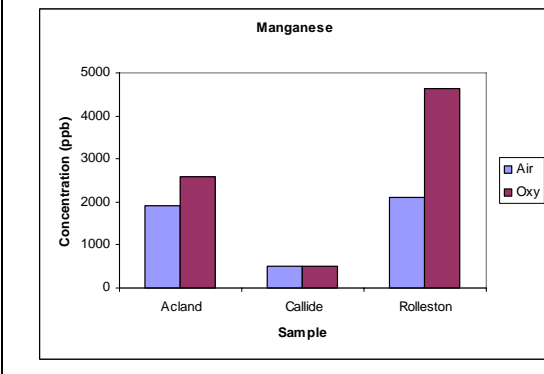
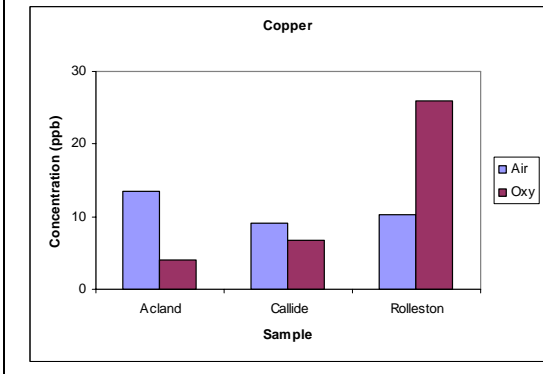
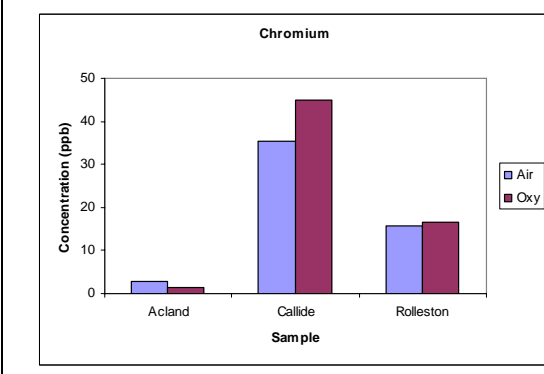
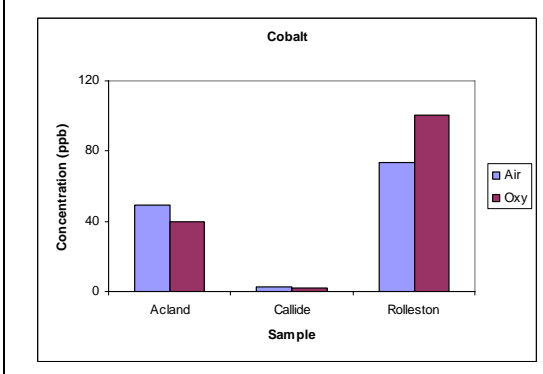
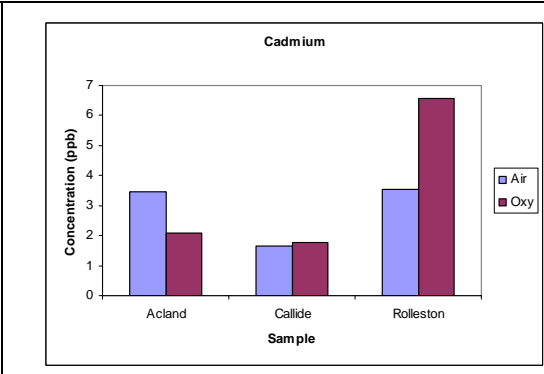
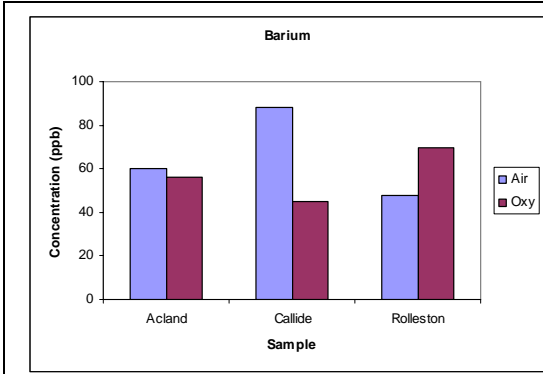




APPENDIX 2. COMPARISON OF THE LEACH DATA ON PAIRED ASHES FROM THE AIR-FIRED AND OXY FUEL COALS

Table 2.1 Leach Data on Paired Ashes from the Air-fired and Oxy Fuel Coals (I:s = 3.5:1)





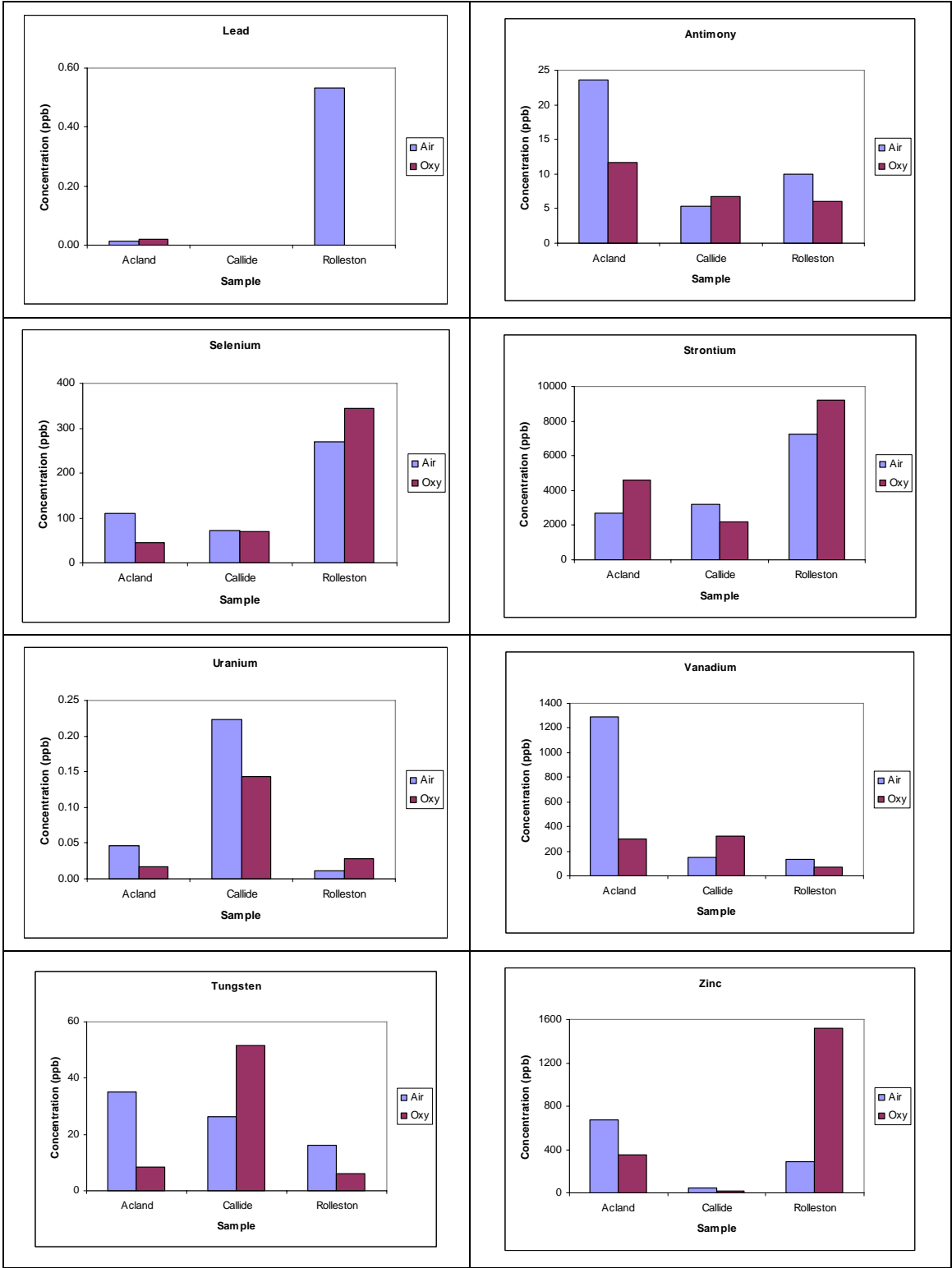
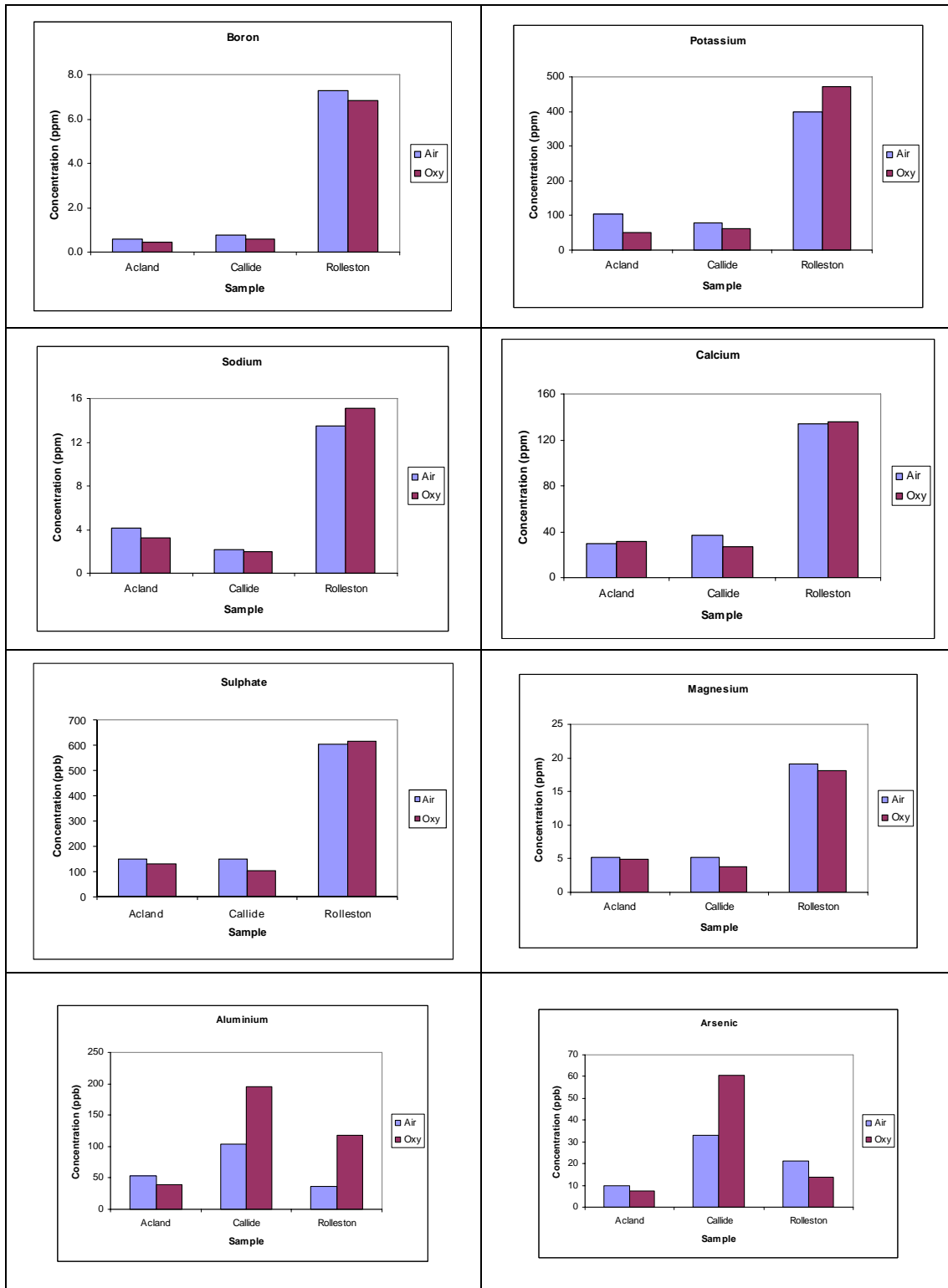
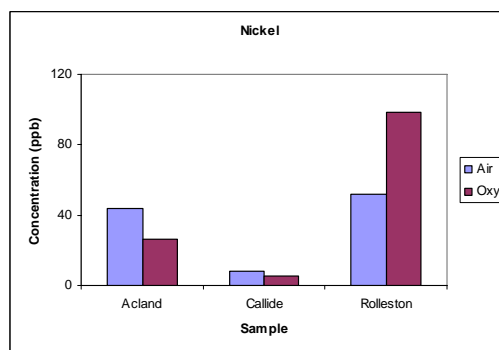
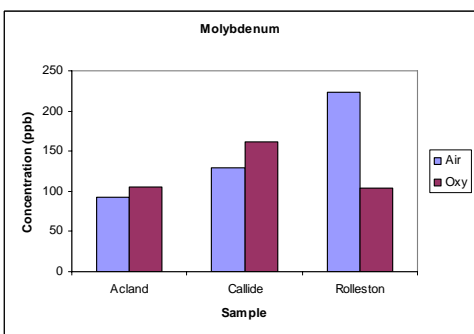
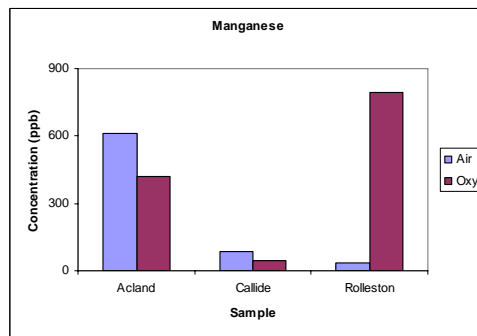
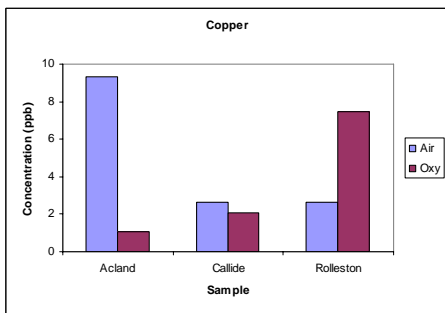
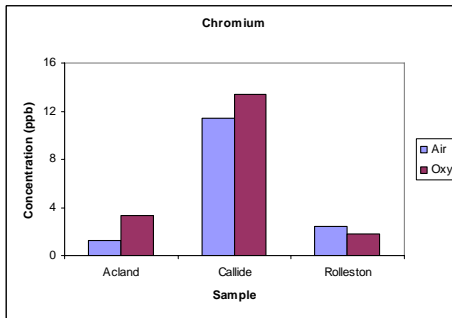
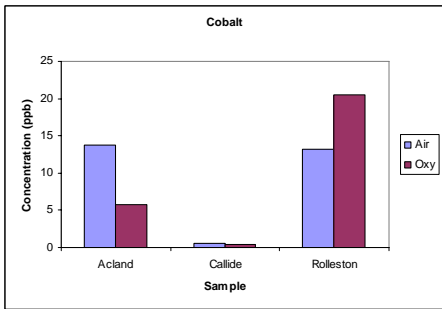
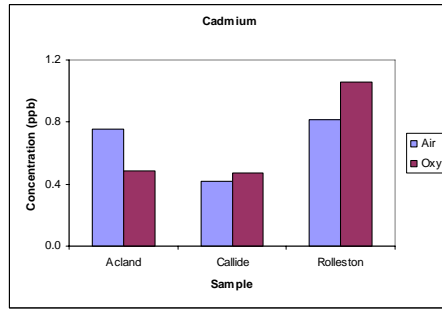
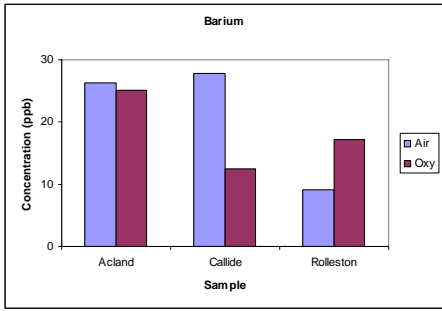
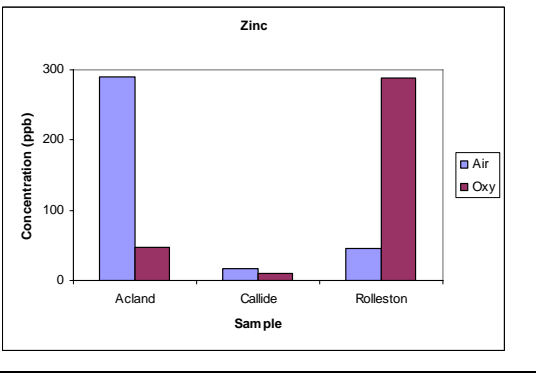
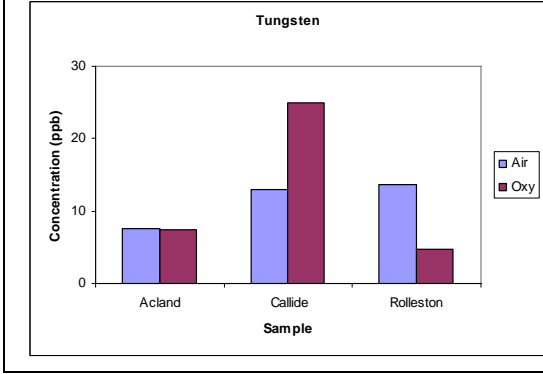
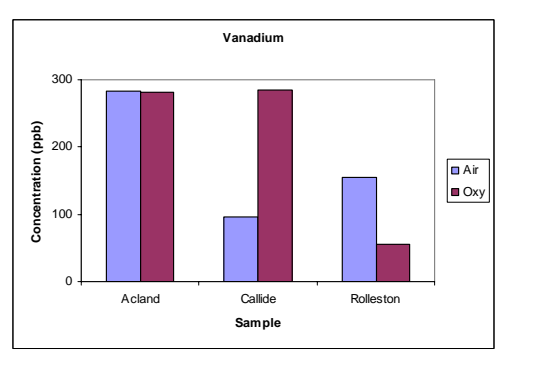
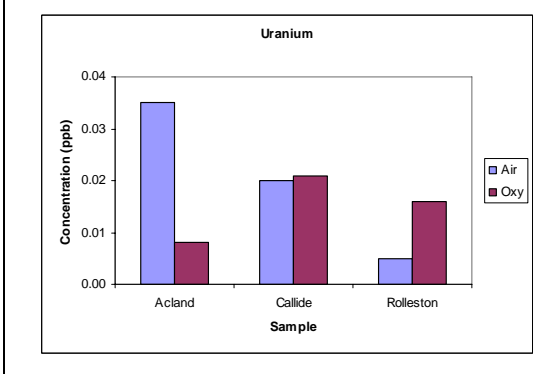
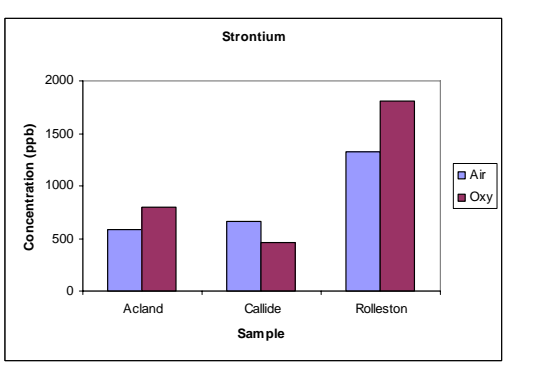
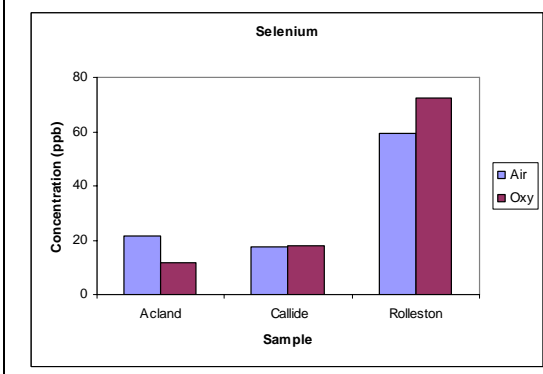
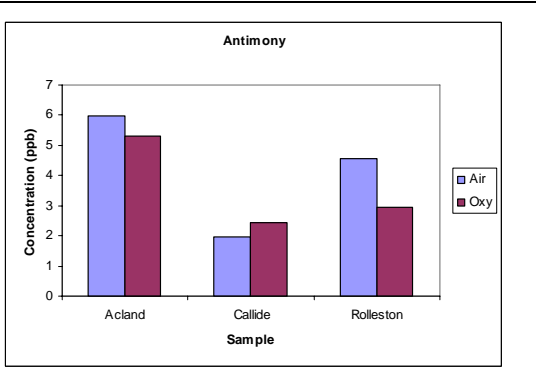
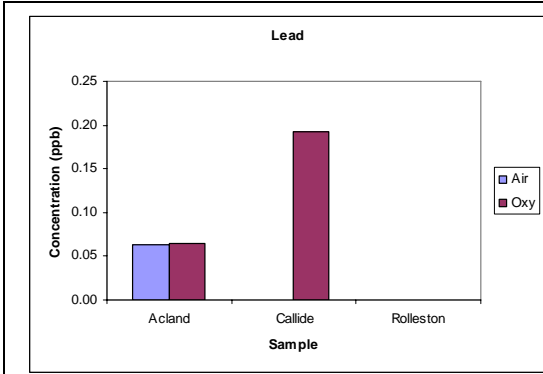


Table A2.2 Leach Data on Paired Ashes from the Air-fired and Oxy Fuel Coals (1:s ratio of 20:1)

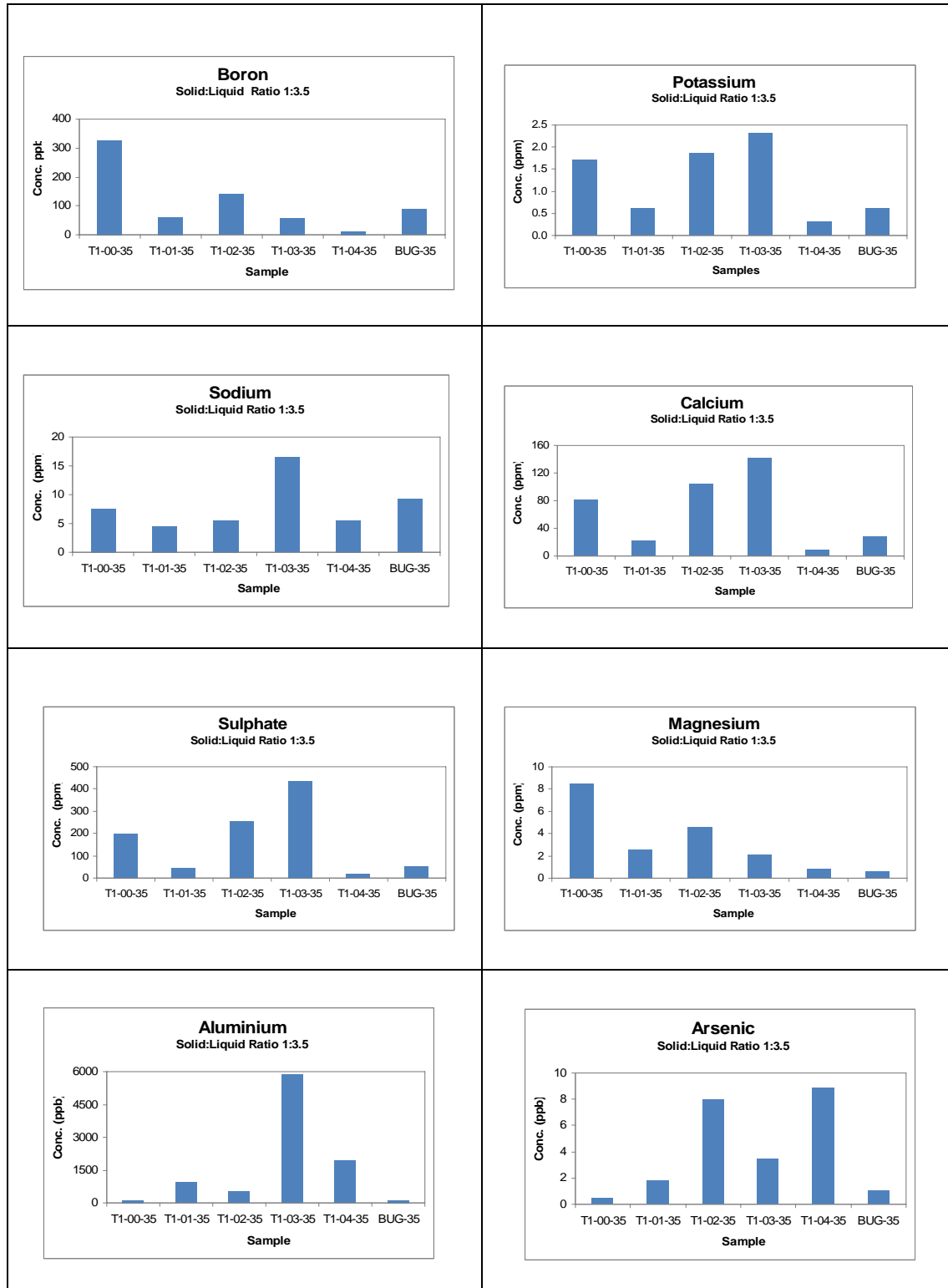


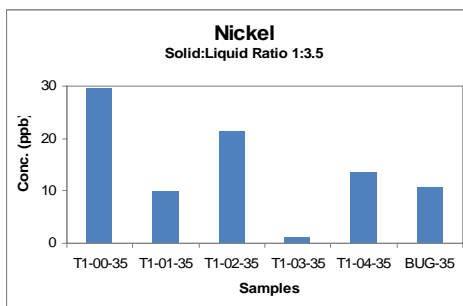
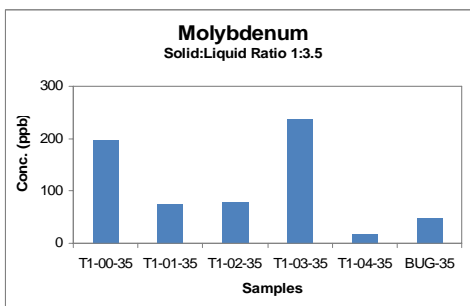
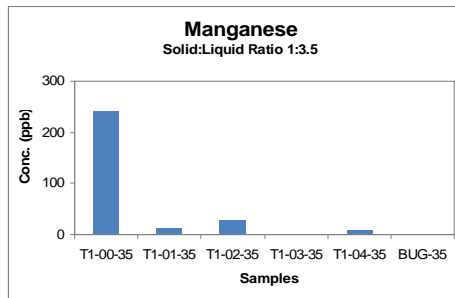
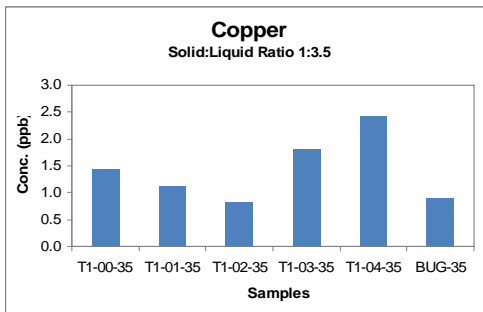
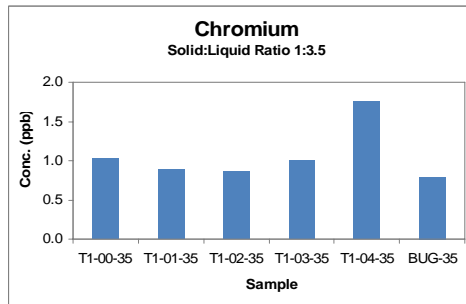
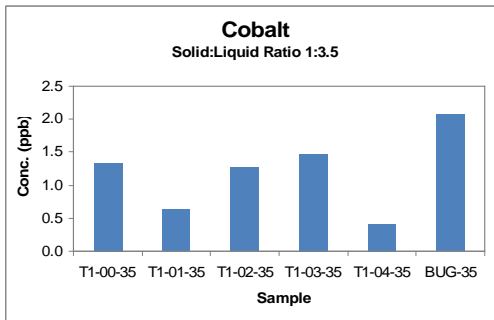
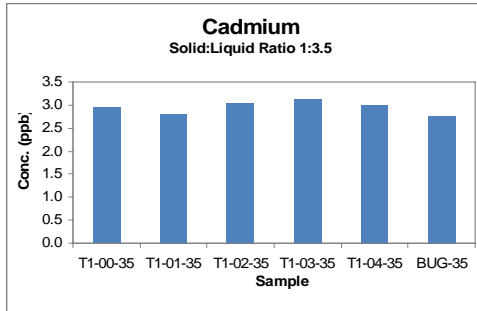
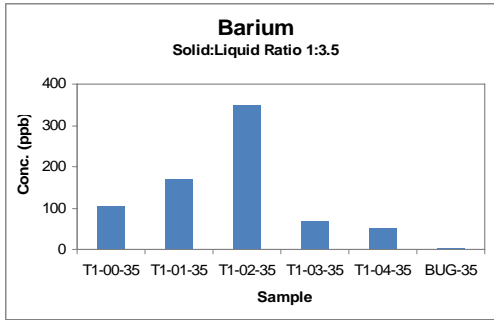




APPENDIX 3. COMPARISON OF LEACH DATA FROM GASIFIER SLAGS

Table 3A.1 Leach Data on Slags from German Tests and Buggenum (l:s = 3.5:1)





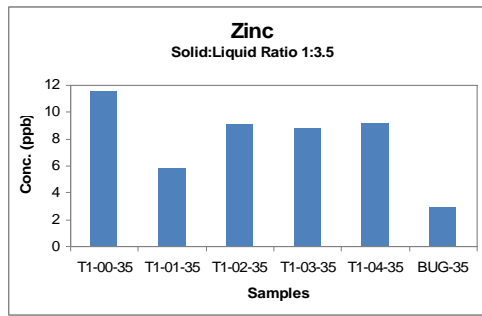
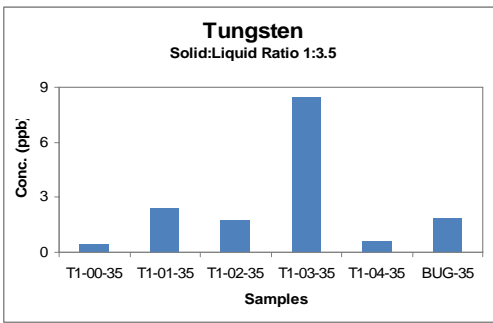
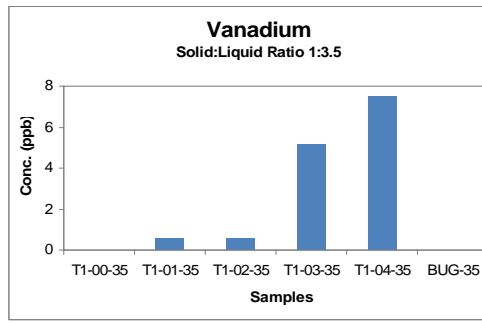
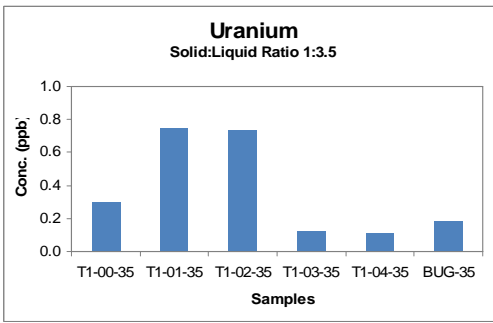
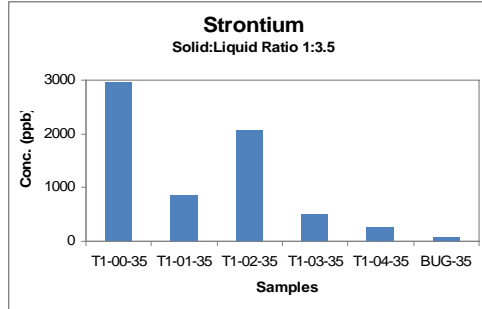
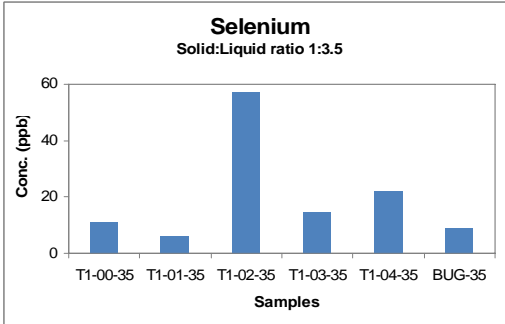
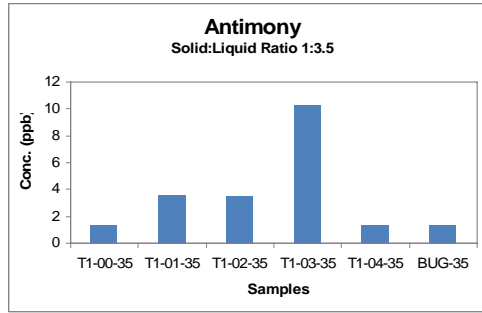
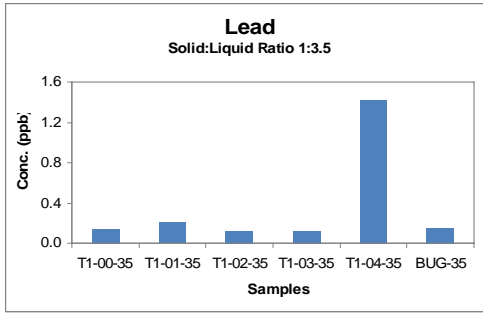


Table 3A.2. Leach Data on Slags from German Tests and Buggenum (l:s ratio of 20:1)

