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SUSTAINABLE DISPOSAL OF COAL PROCESSING WASTE STREAMS

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Mohammad Rezaee, Student

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SUSTAINABLE DISPOSAL OF COAL PROCESSING WASTE STREAMS

DISSERTATION

A dissertation submitted in partial fulfillment of the
requirements for the degree of Doctor of Philosophy in the
College of Engineering
at the University of Kentucky

By
Mohammad Rezaee

Lexington, Kentucky

Director: Dr. Rick Q. Honaker, Professor of Mining Engineering Department

Lexington, Kentucky

2015

ABSTRACT OF DISSERTATION

SUSTAINABLE DISPOSAL OF COAL PROCESSING WASTE STREAMS

Modern coal preparation facilities incorporate a wide array of solid-solid and solid-liquid separation processes for rejecting mineral matter to meet market specifications. The coarse mineral matter is typically placed into engineered refuse piles whereas the fine refuse is either stored in impoundments or co-disposed with the coarse refuse. The discharge water from the refuse material represents an environmental concern due to the potential release of trace elements, and the subsequent elevation of total dissolved solids and conductivity. The research findings reported in this dissertation addresses sustainable coal processing waste disposal through using strategies aimed at minimizing the environmental impacts. To provide an accurate and inexpensive method to assess the potential environmental effects of a given waste material, a conductivity screening-level test was modified to incorporate the impact of particle surface area. The test was used on various waste streams as well as the particle size and density fractions of each waste stream to identify environmentally sensitive components that can be separated from the bulk and isolated to prevent negative environmental impacts. The results were subsequently evaluated for long term mobility of trace elements under different disposal scenarios: (i) static leaching tests designed to simulate the quiescent conditions in a stable impoundment, and (ii) a dynamic test to simulate waste materials exposed to the atmosphere in variable wet/dry storage conditions. The results indicated that liberating, separating and isolating the highest density fractions (>2.68 SG) which represents less than 5% of the coal refuse materials results in significant abatement of total dissolved solids and conductivity. Required modifications of the coal processing plants were suggested to segregate and subsequently isolate the environmentally sensitive fractions from the remaining refuse material.

Keywords: Waste Disposal, Coal Processing, Leaching, Trace Elements, conductivity

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SUSTAINABLE DISPOSAL OF COAL PROCESSING WASTE STREAMS

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This Work is dedicated to the memory of my father and mother who have always inspired me to peruse my dreams.

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1. INTRODUCTION AND BACKGROUND

Upgrading of coal, which occurs after mining and before transport of the cleaned product to market, is achieved using low-cost facilities that incorporate a variety of solid-solid and solid-liquid separation processes. The process is driven by financial incentives resulting from reduced freight costs and improved utilization properties for the product coal. While these benefits are well documented, the coal industry often overlooks the important role of coal preparation in environmental control. In fact, coal processing facilities have long played a critical role in reducing the emissions of pollutants at coal-fired power stations. Airborne pollutants impacted by preparation include solid particulates such as fly ash as well as gaseous emissions of precursors associated with acid-rain and air toxics. These emissions are strictly regulated for coal-fired utilities by the EPA through various legislative acts such as the 1990 Clean Air Act Amendment (CAAA) and 2005 Clean Air Interstate Rule (CAIR). Many of the air pollutant precursors identified in the CAAA are associated with the mineral matter commonly rejected by coal preparation plants. Some of the most noteworthy of these are antimony (Sb), arsenic (As), beryllium (Be), cadmium (Cd), chlorine (Cl), chromium (Cr), cobalt (Co), fluorine (F), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), selenium (Se) and radionuclides.

During combustion at coal-fired utilities, these elements may be released to the atmosphere as solid compounds with the fly-ash and in the vapor phase with the flue-gas. The pre-combustion rejection of trace elements by coal preparation is attractive since the waste rock is coarser and has a lower reactivity than the high-surface-area ash generated by power stations (Jacobsen et al., 1992). In-plant sampling campaigns conducted by various researchers (Luttrell et al., 2000) suggest a good correlation between the rejection of mineral matter and the removal of trace elements during physical cleaning. These findings are also supported by laboratory float-sink tests performed using a variety of eastern U.S. coals (Palmer et al, 2004). These data suggest that trace elements are typically rejected at levels of 40-70% by weight using conventional preparation technologies.

Unfortunately, the current focus of coal preparation facilities is not on addressing water-related environmental problems. As such, many experts working in this technological area now believe that a new function to deal with comprehensive environmental management of air and water should be added to the list of responsibilities for coal processing facilities. There exist additional opportunities for redesigning preparation facilities for (i) the characterization, handling, disposal and storage of solid wastes and for (ii) the monitoring, transport, treatment and discharge of mine-influenced waters over the entire life cycle of mining projects. Preparation operations are ideally suited to provide the opportunity to address a multitude of environmental issues related to the coal mining system. In particular, the possibility of manipulating coal processing unit operations to minimize short- and long-term water discharge of regulated constituents offers great potential. These new functions can be accomplished through the addition of new steps aimed at eliminating environmental problems.

Research is also needed to spearhead the development of new coal processing technologies that can improve how mine waste is managed, handled and disposed near the working face of underground or surface mines. Current practices in Central Appalachia require an extensive amount of rock to be extracted from roof and floor material. After processing, 50-70% of the run-of-mine material is rejected and placed into surface storage areas. Recent research has shown that this out-of-seam material is a primary source of trace elements that can be released to the environment. The development of a new generation of separation technologies that are capable of removing a significant amount (40-60%) of the rock material as close to the working face as possible and storing the material underground/in-pit could significantly reduce the footprint of the mining operation and reduce other environmental issues associated with releases of surface waste storage facilities. Underground storage of waste may also provide potential to reduce other environmental issues, such as those caused by subsidence. Also, according to recent research at National Institute for Occupational Safety and Health (NIOSH), waste storage behind seals could provide an effective barrier to absorb energy from accidental explosions in sealed areas of an underground mine.

On the other hand, coal and coal by-products (processing waste and combustion waste streams such as fly ash and bottom ash) are source of many valuable elements such as rare earth elements (REE), and precious metals, e.g. Germanium, as well as industrial metals. It has been estimated that the U.S. needs for REE can be met from the processing of the waste streams generated from the treatment of heavy mineral sand, phosphate, iron and copper ores, coal and coal combustion facilities (fly ash and bottom ash). REE recovery as a byproduct provides significant economic advantages as mining operations that recover REE as the primary product have been disadvantaged by low cost operations outside the U.S. The Mountain Pass mine in California is the only operation in the U.S. that focusses solely on REE production and is currently struggling to be competitive with international sources. If REE were extracted as a byproduct from the aforementioned sources, mining operations such as Mountain Pass would not be needed thereby reducing the environmental impacts from extracting REE from a primary source.

The recovery of REE from secondary sources could also be significantly beneficial to the economics of an operation that currently struggles to meet current profit demands from the production of their primary product. There are many examples whereby the revenue from the primary product meets the cost of operating the facility and the revenue from the secondary source(s) provides the profit for the operation.

As a results, sustainable disposal practices of coal processing waste materials is suggested to be the most effective strategy, from which valuables can be recovered for commercial use while the remaining materials are processed to generate environmentally benign material. Sustainability of our national resources is critical for our economy, the environment and our independence. Utilizing the materials that we extract from mining operations to their fullest while also using state-of-the-art technologies to minimize environmental impacts is of utmost importance for our society.

Sustainable coal waste disposal may require following steps:

1) Discovering the mode of occurrence of hazardous trace metals, REE, precious and industrial elements in coal and their fractionation in processing plants.

2) Developing and conducting characterization tests to determine the association between trace elements of environmental concern and various forms of minerals that are present in run-of-mine coals. These tests could be conducted to specifically identify these associations as a function of material properties that can be exploited for separation (e.g., particle size, density, magnetic susceptibility, etc.).
3) Formulating the low cost operations for segregation of hazardous fraction from valuable fractions and possible scenarios for isolation/encapsulation of the hazardous fractions.
4) Formulating modifications of the coal processing plants for extraction of valuable minerals and elements from the remaining waste materials.

For improving the sustainability of coal processing waste disposal practices, this research focused on the minimizing the environmental impacts of coal waste disposal through the identification and isolation of the hazardous fractions. To achieve this goal, precise and reproducible short leaching characterization tests were developed to identify environmental concerns of coal waste disposals as a function of material properties. The results were then analyzed for long term through conducting leaching experiments, which were designed to simulate various storage conditions of the coal waste streams. The findings were then utilized for formulating the required modifications for liberation, and segregation followed by isolation of the environmental concerned fractions.

1.1 Coal Mining and Regulations

Coal mining has been an important source of fuel and energy in the United States with an estimated 250 billion tons of recoverable resources in North America alone (EIA, 2007). In order to utilize coal and increase its combustible recovery, the waste components, which consist largely of incombustible mineral matter, are separated from the coal by coal cleaning process. The generated refuse material from the cleaning process must be stored or disposed of in an environmentally acceptable manner as specified by existing federal and state environmental regulations and permits. According to the U.S. Department of Energy, 92% of coal consumed in 2003 was used for electricity generation, and that share is expected to rise to 94% by 2025.

The products of both coal cleaning and utilization are covered under several federal and state regulations and statutes such as the 1990 Clean Air Act Amendments (CAAA), the Clean Water Act (1977), the Safe Drinking Water Act (1974), the Migratory Bird Treaty Act (1918), the Endangered Species Act (1973), the 1976 Resource Conservation and Recovery Act (RCRA), and 2005 Clean Air Interstate Rule (CAIR), and A Field-Based Aquatic Life Benchmark for Conductivity in Central Appalachian Streams (2011). Some regulations are specific to coal mining such as the Federal Mine Safety and Health Act (1977) and the Surface Mining and Reclamation Act of 1977 (SMCRA).

Of particular interest to the coal mining industry, the Clean Air Act Amendments (CAAA) of 1990 identified eleven trace elements and their compounds commonly found in coal as potentially “hazardous air pollutants” (HAPs). These selected elements are listed in the

Table 2.1. The range of values for each element includes a collection of data from different coal seams and locations with the concentrations expressed as a geometric mean of those ranges.

Table 1.1US EPA Selected elements classified as HAPs under 1990 CAAA (Davidson and Clark, 1996).

Element	Symbol	Concentration (µg/g)	Ranges (µg/g)
Beryllium	Be	2	0.1 – 15
Chromium	Cr	20	0.5 – 60
Manganese	Mn	70	5 – 300
Cobalt	Co	5	0.5 – 30
Nickel	Ni	20	0.5 – 50
Arsenic	As	10	0.5 – 80
Selenium	Se	1	0.2 – 10
Cadmium	Cd	0.5	0.1 – 3
Antimony	Sb	1	0.05 – 10
Mercury	Hg	0.1	0.02 – 1
Lead	Pb	40	2 – 80

The federal mandates in Titles III and IV of the Clean Air Act Amendments of 1990 have placed increasingly stringent demands on the type and grade of coal that can be burnt in an environmentally acceptable manner. This has increased the push for advanced cleaning prior to supply to utility companies. The removal of impurities during cleaning significantly reduces the amount of Hazardous Air Pollutants (HAPs) and this contributes to an effective reduction in emissions during coal firing in the power plant. The waste products of coal cleaning typically consist of quartz, clays and pyrite. While the emissions from coal-fired power plants are subject to further emission control devices that eliminate HAPs from the flue gases to required standards by the US Environmental Protection Agency (EPA), fly ash, the waste generated by the preparation plant, is typically disposed of in tailings impoundments.

1.2 Coal Processing

Coal processing utilizes the low cost separation technologies to fractionate the heterogeneous coal run-of-mine to organic (carbonaceous) and inorganic (mineral) matter to increase heating value and meet the specification of the market such as specific energy, ash and moisture content (Figure 1.1).

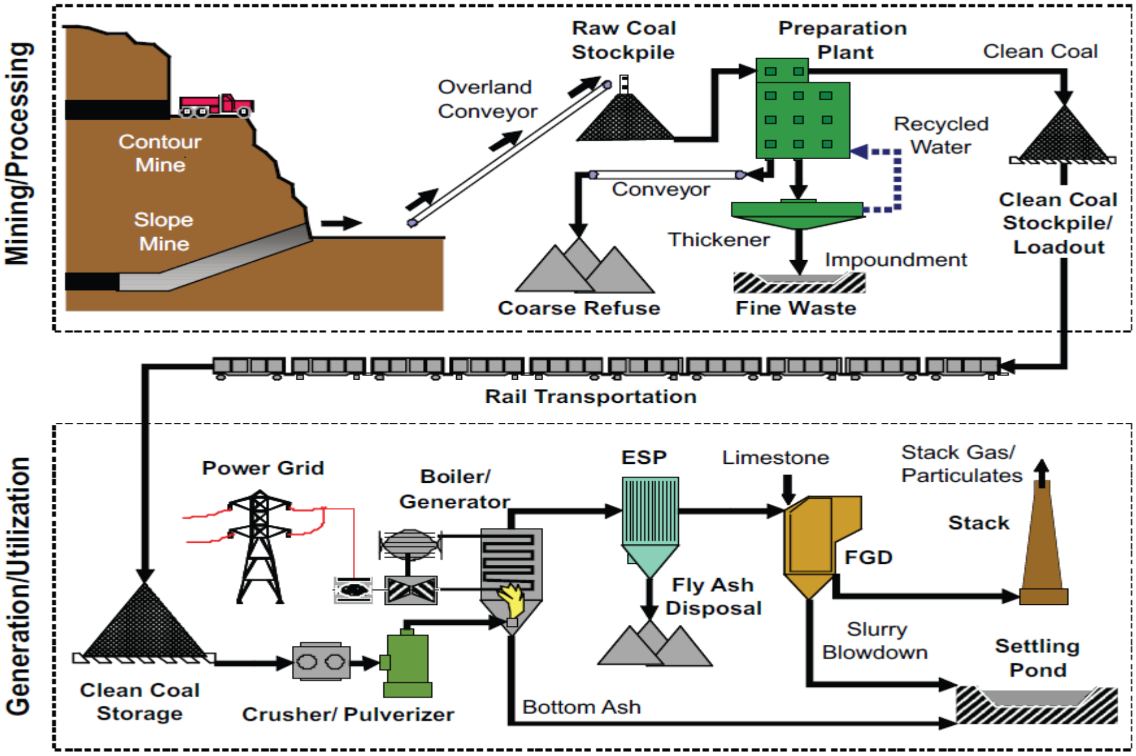


Figure 1.1. Schematic steps from coal mining to utilization (Gluskoter et al., 2009).

Coal processing involves the application of series of particle sizing, cleaning and dewatering units (Figure 1.2). Run-of-mine coal after crushing for partially liberation of organic from mineral matter, is treated in coal processing plants in different particle size fractions. Sizing in the plant is achieved through the application of screens and classifying cyclones. Coal cleaning for coarse (greater than 10 mm) and intermediate (10 x 1 mm) particle size fractions is achieved through utilization of dense medium vessel and dense medium cyclone, respectively. The dense medium separations utilize a dense medium suspension to separate the coal and rocks based on their relative density difference. Fine (1 x 0.15 mm) particle size fraction is typically treated using a series of spiral concentrators which fractionate coal and rock based on the particles size, shape and density. Depending on the amount of materials in the ultrafine (smaller than 0.15 mm) size fraction, froth floatation circuit may be used for coal cleaning in this fraction. Froth floatation utilizes the difference between hydrophobicity of rock and organic materials. Finally, appropriate dewatering units are applied to reduce the moisture content of the final products or recovery of magnetite used in the dense medium circuits. Coal processing, therefore, generates, coarse and fine refuse materials that need to be disposed.

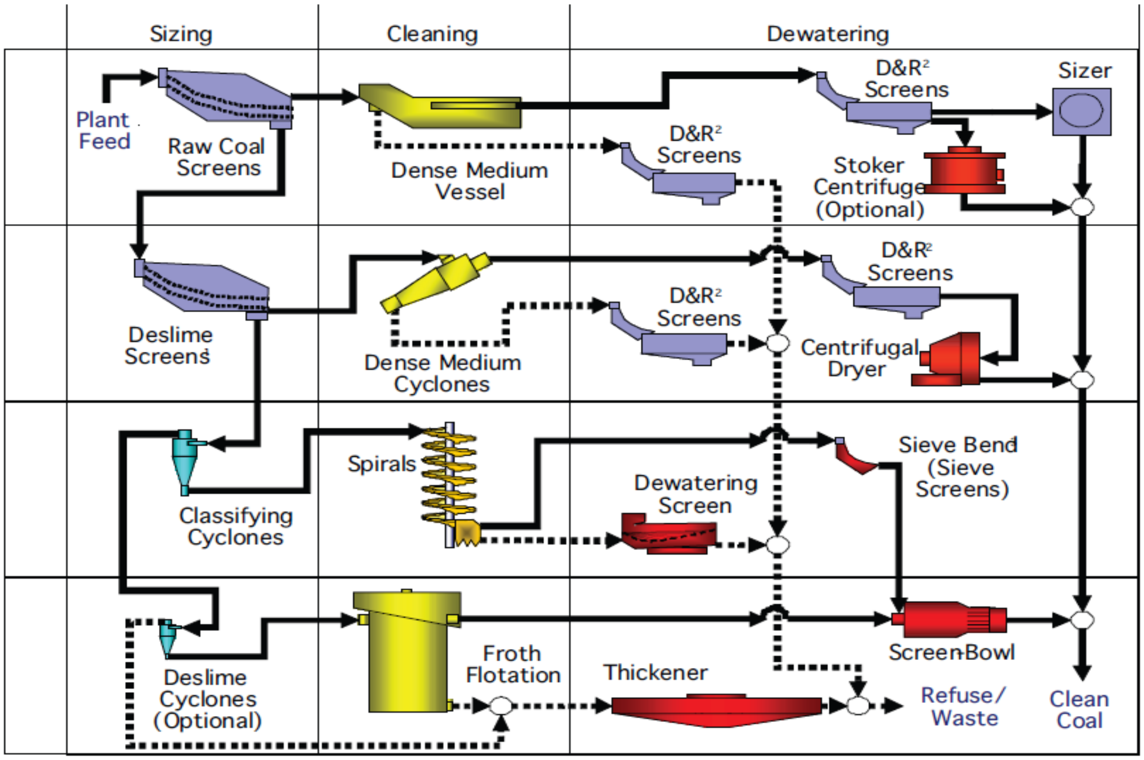


Figure 1.2. Schematic coal processing plant flowsheet

The tailings generated from coal preparation processes are generally exposed to air and water. The interaction of pyrite and other sulfide minerals in the tailings with air and water leads to the production of iron sulfate and oxyhydroxide minerals and sulfuric acid. The acidic conditions generated from such mineral systems enhance the solubility of both major and trace elements in the tailings. The mobilization of such elements may not only increases the conductivity of the aqueous streams but also creates significant problems if allowed to get in contact with the local natural groundwater (Rezaee et al., 2013).

1.3 Coal Waste Disposal

As a result of coal processing for improving the coal heating value and meeting the market specifications, 50-70% of the run-of-mine material is rejected and placed into surface storage areas which are refuse piles or impoundments. Refuse pile are designed to store the coarse refuse materials that can be easily dewatered and hauled by trucks or conveyor belts. Impoundment describes ponds that are used to store mining tailing slurry with high water content by constructing a dam using coarse refuse and sand from previous mining activities. To reduce the cost, the coarse refuse is usually used to dam the opening of a hollow between adjacent mountains near the mining site. Tailings impoundments are also designed to perform other functions in addition to the disposal function. Some of the functions include removal of suspended solids from process water by sedimentation, equalization of wastewater quality, storage and stabilization of process recycle water and so on (Anon., 1987).

Concerns about dust generation, transportation costs, health concerns and performance have resulted in the preference of wet cleaning processes. Therefore, fine coal and mineral matter, waste slurry with large amounts of water are conventionally disposed of in an impoundment. In the US, 713 fresh-water and slurry impoundments were reported to be active by MSHA as of August 2001 (Bentley, 2001). Although impoundments are believed to be the cheapest way to dispose the waste material, dam failures, flooding from breached impoundments, acid mine drainage, spillages and overflows and local groundwater contamination from undesirable leachate generation due to the presence of iron and sulfur in coal refuse materials are considered as potential environmental problems of tailings impoundments. (Alam, 2011; Gardner, J. S., et al., 2004; National Research Council, 2002; Davies, W. E., et al., 1972; Owens, 1987; Michalek etc., 1996).

Many impoundments are getting close to their capacity. Additionally, permits to construct new impoundments are becoming increasingly difficult to obtain, hence, there is an increasing interest in the alternative methods and technologies for disposing the fine coal tailings by reducing the amount of waste generated, utilizing waste, or disposing of the wastes elsewhere (National Research Council, 2002). Fine coal waste generated during coal preparation plants can be reduced or eliminated during both the mining, e.g. selective mining, and the preparation phases. However, implementing options for waste elimination of preparation plant is easier during coal preparation than mining, due to extraction of many low quality coal seams.

Different alternatives or strategies may be applied for the impoundments. Such strategies are adding fine coal waste to the cleaned coarse coal product, dewatering the slurry product solidifies (to a degree) and reducing the volume of the waste (Osborne, 1988; Leonard, 1991), use of coal water slurry as fuel for traditional combustors or gasifies (Syngle and Sinn, 1991; Harrison and Akers, 1997; Arey,1997; Couch, 1998; Rousaki and Couch, 2000; DOE, 2001), disposing of fine coal waste in surface fills and underground workings (National Research Council, 2002) , co-disposing fine and coarse rejects (Williams et al., 1990, 1992, and 1995), solidification of fine coal stream (Malone & Jones, 1979; Cullinane et al.,1986; Cullinane & Jones, 1986; Wetzman, et al. 1988; Barth et al., 1990; Conner, 1990; Dermata & Meng, 1995; Glasser, 1997; Poon et aI., 1986 & 2004; Jang & Kim, 2000; Leist et al., 2003; Duchense & Laforest, 2004; Bagnoli et al.,2005; Amini, H. R., et al., 2008), adding lime or fly ash to fine coal stream (Adams, 1972; Stewart et al., 1997; Jang & Kim, 2000; Shang et al., 2006), and remining slurry impoundment (National Research Council, 2002). Some of these strategies add cleaning responsibilities to the power plants.

Oxidation and dissolution of mineral content of coal refuse streams may result in acid mine drainage, release of trace elements into the supernatant liquids and elevation of total dissolved solids and electrical conductivity of the discharged water. Such discharged water requires physical and chemical treatment to minimize the total dissolved solids and conductivity level, especially in cases which there may be the risk of pollution of head water streams. Spesefic conductance values of water exceeding 500 μS/cm in headwater streams has been reported as one of the causes for the loss of certain groups of bugs, e.g. myflies, and the disturbance of aquatic life in Appalachia (Cormier *at al.*, 2011; Agouridis *at al.*, 2012) . Therefore, developing strategies aimed to minimize environmental concerns regarding coal mining and processing waste disposal increases the sustainability of coal mining.

1.4 Trace elements

Trace elements are defined as elements with a concentration of less than 1000 ppm (µg.g-1) in dry coal, as expected for naturally occurring materials formed under varying conditions over a long period.

In addition to the environmental aspect of trace elements, there are several other reasons to work on coal trace elements. During coal mining some trace elements may be mobilized, especially under oxidizing conditions which affect pyrite, thereby producing acid conditions (Swaine, 1978a). This redistribution of trace elements might result in changing the concentrations of some trace elements in nearby surface and underground waters and in the overburden. These possible changes should be considered when rehabilitation of an area is undertaken, especially in the case of pastures and grazing animals, where deficiencies or excess of some elements may be problematic. They may also lead to significant risks to aquatic and semi-aquatic organisms. Such effects could be either as subtle as minor physiological changes or as drastic as extirpation of entire populations. (Rowe et al., 2002)

Trace elements also are related to several practical situations like: the requirement of less than 2 ppm boron in carbon used as a moderator in nuclear reactors (Hutcheon, 1953), the interest in boron in certain steels is due to its effect on mechanical properties (Borrowdale et al, 1953), and also embrittlement in steel due to arsenic and phosphorus. (Kurmanov et al., 1957; Steven and Balajiva, 1959). Coal and fly ash also could be the source of several elements like: germanium (Goldschmidt, 1930 and 1935), gallium (Inagaki, 1956), selenium (Goldschmidt, 1954), cobalt (Kuhl, 1957), uranium (Berkovitch, 1956).

Trace elements of environmental concern are listed under both the 1990 CAAA and the 1976 RCRA statutes. Swaine (1990) also provides an assessment of the environmental hazard posed by specific trace elements during coal utilization. The listing in Table 2.2 shows a group of 7 trace elements categorized as "prime interest" (As, Cd, Cr, Pb, Hg, Ni, and Se), followed by a group of 6 of intermediate priority (Sb, Be, Co, Mn, Th and U) and the remaining 11 of lesser concern.

Also PECH (1980) categorized the elements into the following six groups:
Elements of greatest concern (As, B, Cd, Hg, Mo, Pb, Se);
Elements of the moderate concern (Cr, Cu, F, Ni, V, Zn);
Elements of minor concern (Ba, Br, Cl, Co, Ge, Li, Mn, Sr);
Radioactive elements, these are generally considered to be of minor concern, but adequate information is lacking for a proper assessment, (Po, Ra, Rn, Th, U);
Elements of concern but "with negligible concentration in coal and coal residues" (Ag, Be, Sn, Tl);
Elements of "no immediate concern".

Table 1.2. Trace elements of environmental concern in coal utilization

Element	1976 RCRA	1990 CAAA	Swaine’s Assessment (1990)	
			“Prime Interest”	“Some Interest”
Antimony, Sb		Yes		Yes
Arsenic, As	Yes	Yes	Yes	
Barium, Ba	Yes			
Beryllium, Be		Yes		Yes
Boron, B				Yes
Cadmium, Cd	Yes	Yes	Yes	
Chlorine, Cl				Yes
Chromium, Cr	Yes	Yes	Yes	
Cobalt, Co		Yes		Yes
Copper, Cu				Yes
Fluorine, F			Yes	
Lead, Pb	Yes	Yes	Yes	
Manganese, Mn		Yes		Yes
Mercury, Hg	Yes	Yes	Yes	
Molybdenum,				Yes
Nickel, Ni		Yes	Yes	
Selenium, Se		Yes	Yes	
Silver, Ag	Yes			
Thallium, Tl				Yes
Thorium, Th		Yes		Yes
Tin, Sn				Yes
Uranium, U		Yes		Yes
Vanadium, V				Yes
Zinc, Zn				Yes

*Elements in bold occur on at least two lists, including Swaine’s “prime” interest list, elements in italics occur in two lists, including Swaine’s “some” interest list.

1.5 Origin of trace elements

The origin of trace elements in coal is in part attributable to the peat formation stage, in which the uptake of certain elements by plants are removed by ion exchange from swamp water, and in part to some mineral matters added from incoming waters and the atmosphere, and minerals formed in situ. Additions of minerals depend on some factors like the types of the nearby rocks, weathering and the means of transport to the peat area, and changes in pH, which can enhance the retention or removal of trace elements. (Cohen et al. 1987; Baas Becking et al., 1960; Cecil et al. 1982; Cairncross and Cadle, 1988). It is clear that trace elements in coal have been influenced over long period of time by botanical, geological, biological, biochemical and chemical sources. (Swaine, 1990). As a result, the mode of occurrence of trace elements could be both mineral associated and organic associated (Smyth, 1966; Finkelman 1981, 1982, 1988, and 1994; Cecil et al., 1981; Harvey and Demaris, 1987; Swaine, 1990).

1.6 Mode of occurrence of trace elements

The mode of occurrence is an important factor in determining the behavior of a given element during cleaning processes and many researchers have worked on how elements partition among different fractions in coal cleaning processes. Figure 2.1 classifies the modes of occurrence of trace elements in coal (Clarke and Sloss, 1992; Vejahati et al., 2010).

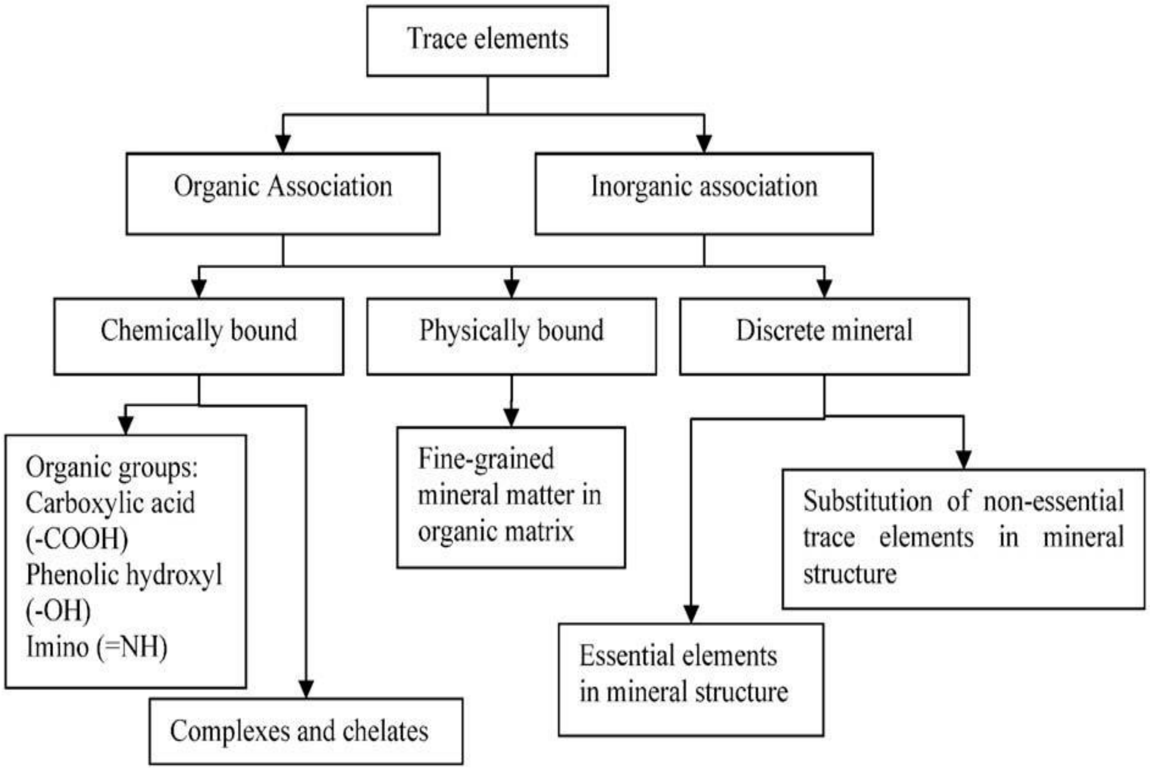


Figure 1.3- Mode of occurrence of trace elements

Querol et al. (1995) performed an extensive study on trace element distributions in both coals and wastes. Table 1.3 shows the summary of their funding (Vejahati et al., 2010).

Table 1.3. Trace elements distribution in coal

Affinity	Mineral Group	Mineral Type	Elements
Inorganic	Clay minerals and feldspars	Kaolinite, Illite Montmorillonite	Al, Ba, Bi, Cr, Cs, Cu, Ga, K, Li, Mg, Na, Ni, P, Pb, Rb, Sn, Sr, Ta, Th, Ti, U, V, Y, and rare earth elements
	Iron sulfides	Pyrite, Sphalerite	As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, Se, Ti, W and Zn
	Carbonates	Calcite, Dolomite, Ankerite, Siderite	Ca, Co, Mn
	Sulphates	-	Ba, Ca, Fe, and S
	Heavy minerals	Tourmaline	B
Organic	N, S, Be, B, Ge, V, W, Zr, rare earth elements		

Trace elements are usually associated with one or other of the major minerals, pyrite or illite. These minerals are usually targeted for removal in coal cleaning processes in order to reduce the coal sulfur and ash contents and they typically host many of the trace elements (As, Cr, Mn, Ni, Se, etc.) that are considered hazardous. One of the first systematic methods to determine elemental modes of occurrence is interpretation of analytical data on trace elements in raw coals and in fractions prepared from the coals by float-sink methods (Zubovic, 1966; Gluskopter et al., 1977; Wang et al., 2009).

These data are usually presented in the form of washability curves, which show variations in the concentration of elements as a function of the specific gravity of the separated fraction. Zubovic (1966) used “organic affinity” of an element as a tool which is basically a measure of the degree of association of an element with the organic fraction of the coal. Gluskoter et al. (1977) also used washability curves and organic affinity to determine elemental occurrences in a wide range of U.S. coals. Because of the different washability characteristics of the coals, values for organic affinity for a given element in different coals have little or no basis for comparison. Furthermore, sequential leaching methods results, in which fractions are created chemically rather than physically, armed with quantifying coal mineralogy by X-ray diffraction (XRD) with Rietveld analysis (Mandile and Hutton, 1995; Dale et al., 1997; Huggins et al., 1996, and 2002) , automated scanning electron microscopic methods (see reviews by Skorupska and Carpenter, 1993; Huggins, 2002), or by results of speciation of a number of elements has been determined by X-ray absorption fine structure (XAFS) spectroscopy (Huggins et al., 1993, and 1996) may be helpful to obtain quantitative mineralogical information and determination of trace element behavior in physical coal fractionation methods (Huggins et al., 2002, 2008, and 2011).

Environmentally concerned trace elements and rare earth elements (REE) along with their mode of occurrence in coals are discussed in more detalis here.

1.6.1 Antimony

The presence of antimony (Sb) in coal seams was reported by Daubree in mid-nineteenth century (Briggs, 1934) and it is often determined nowadays, although at its typically low concentrations found in coals it is not considered to be environmentally hazardous. Metal smelting, waste incineration and coal combustion, or emissions from some volcanoes are the main source of Sb in the atmosphere (Austin and Millward, 1988; Cadle et al., 1973). The mode of occurrence of antimony is not well established, but organic association prevails in many coal seams, together with a sulfide association, which may predominate in others. In some coals, Sb was presented as small grains of sulfide, possibly stibnite, which could be associated with organic coal matter (Finkelman, 1981), and therefore, having organic association. Calculated by Sobbioni et al. (1983), mean value of Sb in USA is 0.7 ppm, which is usually much smaller than the mean of Sb for other reported countries except Australia with mean value of 0.5 ppm. (Swaine, 1990)

1.6.2 Arsenic

Before there was interest in trace elements, arsenic (As) was found in some of European coals (Daubree, 1858; Percy 1875), but Goldschmit and Peters (1934) were the first researcher to carry out much investigation on this element. The range of As contents may vary from 1 ppm to several hundred ppm in coal seams (Minkkinen and Yliruokanen, 1978). The mean value of arsenic content in US coals, calculated by Sabbioni et al. (1983), is 14 ppm which is high compared to other countries like Australia (1.5 ppm), South Africa (4 ppm), and 11 ppm for coals burnt in nine EC countries.

The mode of occurrence of arsenic in coal is predominantly an association with pyrite. Arsenopyrite (FeAsS), as in clay minerals and organically bound As are generally much less common forms. Recent studies of arsenic using XAFS spectroscopy on bituminous and higher rank coals (Huggins et al., 1993) showed distinct occurrence of As in pyrite within a concentration range of 10-2000ppm. The recorded XAFS data showed that most of the As was present as arsenical pyrite, in which arsenic substitutes for sulfur in the pyrite (FeS2) structure. Furthermore, XAFS distinguishes As in pyrite from As in arsenopyrite, FeAsS (Huggins et al., 1993; Huffman et al., 1994). Examination of numerous coal samples indicated the presence of arsenical pyrite rather than arsenopyrite. Their other findings showed the presence of the arsenate [AsO43-] species in coal and that such arsenate species accumulated over time as a result of oxidation of pyrite. In summary, they stated that arsenic in bituminous coals occurs principally as a substitution for sulfur in the pyrite structure, and significant arsenate may also be present as a result of the oxidation of arsenic-containing pyrite (Seidu, 2008).

1.6.3 Beryllium

After the initial investigation of Be in some German coals by Goldschmit and Peters (1932), there was a gap of knowledge and research on this element until results of Canadian (Hawley, 1955) and US coals (Stadnichenko, Zubovic and Sheffy, 1961) were published. For US coals, Be contents from 0.05 to 32 ppm have been reported (Swaine, 1990). Generally Be is considered an organically associated trace element, although in some coals, Be may be present as beryl or associated with quartz and clay (Singh, Singh and Chandra, 1983).

1.6.4 Cadmium

While there may be some beneficial effects of cadmium (Cd) in nutrition, Cd is now an element of prime environmental concern and therefore the levels of Cd in coal and coal related materials are of interest (Swaine 1990). The first information on Cd was reported in German coal ashes (Jensch, 1887). In general the main mode of occurrence of Cd in most coal seems is an association with mineral matter in coal; typically it replaces Zn in the mineral sphalerite (ZnS), but other minor mineral associations, clay and carbonate minerals as well as pyrite may occur. (Gluskoter et al., 1977; Gluskoter and Lindahl, 1973; Finkelman, 1994). Most coals have Cd contents in the range of 0.1 - 3 ppm, while Swanson et al. (1976) reported a mean value of 1.3 ppm for U.S. coals.

1.6.5 Chromium

Chromium is an vital trace element which is required for normal carbohydrate metabolism (Anderson, 1981).The hexavalent state, Cr(VI), is the only form that is considered toxic. The trivalent state, Cr(III), found in almost all coal seams is not toxic. Chromium is regarded as a potentially hazardous element in coal-derived fly-ash mainly because a portion of the concentration may be in the hexavalent oxidation state (Meij and te Winkel, 2001; US EPA, 2009). In U.S. coals of bituminous rank, chromium is generally present in one of two trivalent chromium forms: as a minor component in clay minerals, such as illite, or as small-particle oxide or oxyhydroxide minerals associated with the organic macerals (Huggins et al., 2000). This latter species are postulated to have derived from Cr(III) bonded to carboxyl groups, which have decomposed as the coal experienced increasing metamorphism (coalification) (Huggins and Huffman, 2004).

Occasionally, Cr in coal may also be found in oxide (spinel) phases, especially in coals of above average Cr contents; such occurrences, however, appear limited to situations in which weathering-resistant chromium minerals, such as chromite, have been transported into coal-forming environments from nearby ultramafic deposits (Brownfield et al., 1995; Ruppert et al., 1996; Gluskoter et al.,1977; Finkelman, 1981, Huggins et al., 1999). During pulverized coal combustion, chromium-bearing minerals transform and react with other mineral-derived components to form chromium-bearing crystalline phases and glass (Stam et al., 2011). In the process, a small fraction of the Cr is usually oxidized from Cr(III) to Cr(VI). The range of Cr contents is 0.5 - 60 ppm for most coal seams (Swaine, 1990), and averages about 15 ppm for US coals (Sabbioni et al., 1983).

1.6.6 Cobalt

Although cobalt is subjected to EPA CAAA (1990) regulations, there are no reports of unwanted effects caused by Co during coal mining and usage. There is an inclusive review of all aspects of Co by Smith and Carson (1981). This trace element also has an important role in nutrition and some serious deficiencies in grazing animals have been found (Swaine 1990). Co could be associated with mineral matter in coals (linnaetite, other sulfides, clay) or it could be organic associated, as was reported for US coals. (Finkelman, 1981; Des Cloizeaux, 1880; Goldschmidt, 1954; Firth, 1973; Zubovic, Stadnichenko and Sheffey, 1961; Gluskoter et al, 1977). The Co concentration for most coals is within the range of 0.5 to 30 ppm with a mean of 4-8 ppm (Swaine, 1990), and the range of 0.25 to 43 has been reported for the US coals by Zubovic et al. (1979).

1.6.7 Lead

Exposure to lead (Pb) could give rise to illness in certain situations and therefore there is much interest in Pb regarding health and the environment. Pb was first reported by Jensch (1887) in Upper Silesian coals. There is a little argument regarding the occurrence of Pb in coal. Lead was reported to be associated with mainly with galena (PbS), mineral grains of clausthalite (PbSe), in about 50 percent of the Appalachian Basin coals studied, and in about 10 percent of other samples, and Ba minerals, where Pb can be replace Ba (sulphates, carbonates, phosphates, silicates) (Brown and Swaine, 1964; Finkelman, 1981; Bethel, 1962). It could be associated with some minerals like lead tungstate (PbWO4), lead-barium aluminum silicate, plumbogummite [PbAl3(PO4)2(OH)5·(H2O)], in coals as a minor mode of occurrence. Pyrite is able to contain lead in its structure to some extent (Deer et al, 1962). In some low rank coals lead could be organically associated too. The range of lead concentrations in US coals is 2 - 40 ppm (Swaine, 1990).

1.6.8 Manganese

There is interest in Mn because not only of its biological essentiality but also the probable environmental problems of excess amounts of manganese. However, no serious health or environmental effects of Mn during coal mining and its usage have been reported (Swaine, 1990). Regarding the mode of occurrence of Mn in coal; for low rank coals it is mainly organically bound through carboxylic acid groups (Brown and Swaine, 1964; Benson and Holm, 1985), and in higher rank coals there are several modes, including association with carbonate minerals and clays as major forms, association with pyrite and organically bound Mn as minor sources (Finkelman, 1981).

1.6.9 Mercury

Due to the emission of mercury (Hg) to the atmosphere during coal combustion, and its negative impact on biological systems, there is continued interest in Hg in coal. Hg, seemingly, was first determined in coal by Stock and Cucuel (1934) in German coals.

The modes of occurrence in coal proposed by different authors for mercury include the sulfide (HgS), as well as pyrite-bound Hg, metallic Hg, and organically=-bound Hg. However, due to the very low concentration of Hg in most coals (0.02 - 1.0 ppm), little information on the mode of occurrence of Hg has actually been established by direct methods and interpretation based on indirect methods can be misleading. A study of a group of Illinois coals showed significant Hg association with pyrite, and minor part of Hg occurred in the lightest specific gravity fraction of the coal, leading to the conclusion of a minor organic association (Ruch et al., 1971). Huggins et al. (2008) also found a strong association of Hg with pyrite in US Illinois coal seams. (Gluskoter et al., 1977; Ruch et al., 1974). According to Swaine (1990) Mercury is mainly associated with pyrite for most coals. ‘Finkelman (1994) also agrees that mercury is in solid solution with pyrite stating that epigenetic pyrite probably has more mercury than syngenetic pyrite’.

1.6.10 Nickel

Nickel (Ni) is one of the trace elements subjected to the CAAA (1990) regulations and under some conditions, in relatively high levels of Ni, some plants may be harmed, but this is unlikely to occur on coal mine spoil heaps and it is likely that there would not be significant untoward effects from Ni in coal mining and usage. It also has been considered as ‘a relatively non-toxic elements’ by Underwood (1997) (Swaine, 1990). Regarding the mode of occurrence of Ni in coal, experiments by Horton and Aubrey (1950) and Zubovic et al. (1961) showed a range of intermediate organic affinities. The main modes of occurrence of nickel are probably associated with sulfides and organically associated (Finkelman, 1981; Goldschmidt, 1935; Gluskoter et al., 1977). Nicholls (1968) also suggests that coals with Ni content greater than 3 ppm would have the element associated with the inorganic fraction. Some SEM-EDX work on nickel in minerals by Finkelman (1981) suggested that Ni to be most commonly associated with the sulfides such as galena (PbS), sphalerite [(Zn,Fe)S], pyrite (FeS2) and other complex sulfides (Seidu, 2008), and later he added clays (Finkelman, 1988). Omitting some very high Ni contents (>8000 ppm) reported by Goldschmidt (1937), Jones and Miller (1939), and Vorobev (1940) for some unusual coals, the probable range of nickel concentration in most coals is around 0.5 - 50 ppm (Swaine, 1990; Kolker, 2012).

1.6.11 Selenium

Selenium (Se) is very important from nutritional and environmental aspects. There is evidence that small amounts of Se are essential for good nutrition in humans, as well as medical and biological effects, and Se deficiency could be an important factor of two diseases of endemic cardiomyopathy and endemic osteoartheropathy, by which millions of people may be affected in China. The local high selenium content coals could be the source of Se for the soil and plants (Yang et al., 1983; Levander, 1987; Nas; 1976). There are also several industrial Se applications (Zingaro and Cooper, 1974). On the other hands, selenium enriched plants in certain limited areas, have caused toxic effects on grazing animals. Enriched Se soils could be harmful for some plants. The endemic Se-poisoning in Enshi county of Hubei province, China, is the outstanding case of severe effects on humans (Yang et al., 1983).

Regarding the mode of occurrence of Se, it could occur in coal organically associated, in pyrite and other sulfides (probably in solid solution), in galena as PbSe, at least in some coals and possibly in clays (Wedepohl, 1972; Wandless, 1957; Porrett and Swaine, 1976; Ruch et al., 1974; Carter et al., 1973; Finkelman, 1981). Organic matter rich-shale weathering has been identified as a source of Se in coal mine effluents and also se primarily associated with pyritic minerals (Unrine et al., 2013). The mean value of Se in U.S. coals is 0.5 to 4 ppm (Swanson et al., 1976; Swaine, 1990).

1.6.12 Thorium

Thorium (Th) is radioactive and due to its biological and environmental effects is an interesting trace element to do research on in coal utilization. Regarding its mode of occurrence in coal, it is clearly associated with mineral matter in most coals, mainly as monazite, with lesser amounts in zircon and xenotime. Small amounts of Th perhaps could be associated with iron oxides and clays, as in the case with soil; however, Th is unlikely to be organically associated (Palmer and Filby, 1984; Finkelman, 1981; Swaine, 1990). Th contents in most coals are in the range 0.5-10 ppm (Swaine. 1990).

1.6.13 Rare Earth Elements

Rare earth elements (REEs) are a group of 15 lanthanide elements (atomic numbers 57-71) and two transition metal elements (scandium and yttrium) (Binnemans et al., 2013; Ren et al., 2000 Sui et al., 2013; Binnemans et al., 2013; Ren etal., 2000; Resende, 2010). Promethium (atomic number 61) is extremely rare, and is generally considered not to exist in nature (Sui et al., 2013; Binnemans et al., 2013; Ren etal., 2000; Resende, 2010).

Coal has become an alternative raw-material for many metals and organics. Reports have appeared about the recovery of metals such as gold, platinum, vanadium, iron, and aluminum from coal or coal ash (Zhang et al., 2011; Groppo and Honaker, 2009; Bratskaya et al., 2009). Systematic review of coal deposits as an alternative resource of REEs and the beneficiation method of traditional REEs-bearing mineral both have been published in recent years (Seredin and Dai, 2012; Jordens, 2013).

Many papers regarding the distribution and geochemistry of REEs in coal have proved the existence of REE-mineral matter associations (Birk and White, 1991; Birk, 1989; Dai et al., 2008, 2010a, 2010b; Eskenazy, 1987, 2009; Finkelman and Stanton, 1978; Hower et al., 1999; Karayigit et al., 2000; Seredin 1996; Wang et al., 2008; Zheng et al., 2007). Hu et al. (2006) conducted an investigation to indentify the distribution of trace elements in 50 coal samples from DPR Korea, and the results show that all REEs (except Y) have a strong correlation with ash yield, and LREEs have stronger correlation (r from 0.81 to 0.88) than HREEs (r from 0.72 to 0.82). Birk and White (1991) pointed out that the REEs in the bituminous coal of the Sydney Basin displays strong correlation with the ash content (r from 0.58 to 0.87). Karayigt (2000) reported that LREEs in 13 coal samples from Turkish coal at 95% confidence level correlates positively with the ash yield, while the HREEs show no correlation. Eskenazy (1987) also found that the REEs content increases with an increase in ash content of coal. Apart from the correlation coefficient, the REEs mineral sites have been directly observed via scanning electron microscope (SEM) equipped with energy dispersive X-ray analyzer (EDX) (Birk and White, 1991; Birk, 1989; Dai et al., 2010a; Finkelman and Stanton, 1978; Hower et al., 1999; Seredin, 1996).

For coals with normal REEs contents, these elements are mainly concentrated in accessory minerals (allanite, monazite, xenotime), resistate minerals (monazite, florence, xenotime, zircon) or clay minerals (kaolinite, illite) (Birk and White, 1991; Finkelman and Stanton, 1978; Birk, 1989; Eskenazy, 1987; Dai et al., 2012; Wang et al., 2008; Zheng et al., 2007). Finkelman and Stanton (1978) detected at least four accessory rare-earth minerals (monazite, allanite, etc.) in carbominerite bands of Waynesburg coal. The SEM-EDX survey for Sydney coals detected REEs mainly in discrete phosphate minerals derived from detrital fish bones or resistate clastics (Fig.2.5) (Birk, 1989; Birk and White, 1990, 1991).

According to the positive correlation between REEs and lithophile elements including Si, Al, Ti, Fe and Na, Zheng et al. (2007) concluded that REEs in coal from Huaibei Coalfield, China, are mainly distributed in clay minerals. Similarly, Wang et al. (2008) found that most of the REEs in coal from Antaibao mining district, China, are derived from detrital sources and occur dominantly in kaolinite and illite, and to a lesser extent, in phosphate.

For coals with high REEs content, authigenic REE minerals play a dominant role (Hower et al., 1999; Seredin, 1996; Dai et al., 2008, 2012). Seredin (1996) suggested that REEs mostly occur in REE enriched coal in both authigenic grains of REEs, usually 0.5-5μm in diameter, and adsorbed forms on the organic matter or clay minerals. Hower et al. (1999) found that REEs in coal samples from eastern Kentucky are mainly in the form of REE-rich phosphate, tentatively identified as monazite, which is of authigenic origin judging from the fact that the monazite commonly infills cracks in clays and cells in clarain and vitrain. The monazite occurs in very small (<2μm) irregular shape particles. For the coal of Jungar Coalfield, Inner Mongolia, China, Dai et al. (2012) found that REEs are mainly associated with authigenic kaolinite, goyazite, gorceixite and boehmite.

Extensive evidences have been presented pertaining to the existence of REEs (particularly HREEs) as organic compounds in coal which are summarized as follows:

1) Strong correlation of HREEs have been found with other trace elements, such as Ge, W, and Be, which were proven to be organically fixed, and a similar distribution pattern of REEs was found with Ge in coals as a function of particle specific gravity (Gluskoter et al., 1977; Eskenazy, 1982; Eskenazy, 1987; Seredin, 1996; Seredin et al., 2006).
2) HREEs have been enriched with a decrease in the content of clay (coaly clay) rocks, and the LREE/HREE ratio increased with a rise in specific gravity, which indicates that coal with low ash content has an enriched level of HREEs (Yershov, 1961; Seredin, 1996; Eskenazy, 1987; Birk and White, 1991; Wang et al., 2008; Eskenazy 2009).

3) Larger correlation coefficients have been obtained with La, Ce, Sm and Eu (LREEs) compared to the correlation coefficients with Tb, Yb and Lu (HREEs). Also, smaller correlation coefficients exist between HREEs and ash content as well as terrigenous elements (Si, Al, Fe), compared with LREEs (Eskenazy, 1987; Birk and White, 1991; Hu et al., 2006).
4) In organic solvent extraction of coal, the LREE/HREE ratio in the leachate is normally smaller than that of coal, and HREEs complexes with organic matter are more stable than those of LREEs (Birk and White, 1991; Wang et al., 2008; Karayigt, 2000).
5) The mechanism of bonding the REE ions by organic matter can be sorption on the coagulating humic and fulvoacids, as well as formation of organometallic complexes. (Birk and White, 1991; Eskenazy, 1987; Wang et al., 2008)

Based on these findings, it is apparent that HREEs show greater organic affinity than LREEs. Based on the washability data, Gluskoter et al. (1977) calculated the organic affinity for REEs. The organic affinity for La to Ce ranges from 0.08 to 0.75, while for Yb and Lu it ranges from 0.29 to 0.75. Binding of REEs with humic substance (HS) has been recently quantified using Capillary Electrophoresis-Inductively Coupled Plasma Mass Spectrometry (CE-ICP-MS) (Stern et al., 2007; Sonke and Salters, 2006). The binding constant (logKc,LnHA) ranges from 8.9 to 16.5, indicating a strong REE-HS interaction, and displays a lanthanide contraction effect, which is a gradual increase of Kc,LnHA from La to Lu by 2-3 orders of magnitude as a function of decreasing ionic radius (Sonke and Salters, 2006). This implies that the mechanism of binding the REE ions by organic matter in coal can be sorption on the coagulating humic and fulvoacids (Eskenazy, 1987).

There have been conflicting opinions as to what extent REEs are bound with organic matter. The most common view is that REEs associated with the organic matter is only considered a minor part of the total REEs (Dai et al., 2002; Finkleman, 1982; Eskenazy, 1987; Birk and White, 1991; Zheng et al., 2007; Wang et al., 2008).

1.7 Dissertation Outline

For sustainably disposing coal waste streams, this research addresses developing strategies for minimizing the environmental issues regarding coal waste disposal such as minimizing release of trace elements, total dissolved solids and conductivity level of supernatant waster in contact with the streams.

To achieve the target goals, in the second chapter the effect of surface area, leachant volume to surface area ratio and amount of oxidant on electrical conductivity was assessed through conducting a parametric study. The results of parametric study was then used to develop a quick and inexpensive test for conductivity screening-level of waste streams.

In the third chapter, the conductivity screening-level test was used to assess the electrical conductivity of supernatant liquids in contact with various coal refuse streams to identify the significance of each stream in mitigation of elements to the leachant and elevating the totals dissolved solid and conductivity level of the leachate. Electrical conductivity of the leachate was then studied as a function of material properties that can be exploited (i.e., size and density) for the separation of fractions generating high electrical conductivity in contact with water.

Long term leaching characteristics of coarse and fine refuse streams from three processing plants treating low, medium and high pyritic coal seams were evaluated in the fourth chapter. This investigation of the mobility (leachability) of major and potentially hazardous trace elements from coal processing waste materials was conducted using two types of leaching tests. One test, termed the static test, was designed to simulate stable storage of wastes entirely under water, whereas the second test, termed the dynamic test, was designed to simulate storage under more variable conditions that permitted the waste materials to be exposed to air and variations in humidity.

Long term leaching characteristics of material as a function of material properties were examined through conducting column leaching tests, in the fifth chapter. Based on the results, modifications in the coal processing plants for segregation and isolation of environmentally concerned fractions from environmentally benign fractions.

Finally, the conclusions of this study were summarized in the sixth chapter and recommendations for future works were suggested.

2. DEVELOPMENT OF A FIELD LEACHING TEST FOR ELECTRICAL CONDUCTIVITY SCREENING-LEVEL

Summary: A common environmental concern at mining and processing operations is the leaching of trace elements from mining overburden and byproduct streams of coal and mineral processing plants. To quickly assess and compare the potential electrical conductivity values of leachate emanating from various coal processing plant waste streams, research was conducted to examine technical issues associated with the USGS Field Leach Test (FLT) and to modify the procedure and analyses to improve the precision of the test results. The primary issue involves the importance of leachant volume-to-particle surface area ratio in the assessment of the leaching potential for a given source. To determine the key factors impacting leachability of a given material, a statistically-designed parametric study was performed which evaluated the effect of surface area, the leachant volume-to-surface area ratio, and the amount of oxidant on the leaching characteristics of the material. The results revealed that the statistically significant parameters are leachant volume-to-surface area ratio and the amount of oxidizer. Based on the findings of the study, modification to the conductivity screening test was proposed which may be used for the evaluation, prediction and comparison of the leaching characteristics of different materials.

Keywords: leaching, conductivity screening test, surface area, volume to surface area ratio, oxidant, parametric study.

2.1 Introduction

The leaching of major and trace elements into streams and their effect on the environmental state of equilibrium are common environmental concerns especially for mine overburden, coal and mineral processing waste materials, naturally mineralized soil, industrial waste, construction sites, natural and amended soils, ash material from coal combustor units, dust, dried sludge and sediments, etc. (Ghosh et al., 2014; Hageman, 2007; Plumlee et al., 2005; Yager et al.,2004, Van Gosen et al., 2000).

In mining and coal processing, the gangue minerals are separated from valuable minerals or organic material, respectively, using separation technologies which improves the quality of raw material to a level that meets the product quality requirements of manufactures and power generation plants. These minerals may oxidize in the waste impoundments and dissolute into the water. Dissolution reactions of different types of minerals such as sulfide, carbonate and clay minerals have been extensively researched (Evanglou, 1995; Huertas et al., 1998; Köhler et al., 2003; Pokrovskyet al., 2005, Chandra and Gerson, 2010; Bibi et al., 2011). The dissolution of minerals in aqueous streams may result in pH variations and an elevation in total dissolved solids (TDS) in the supernatant water that is in contact with the solid material. The relative level of TDS concentration can be indirectly measured by the electrical conductivity (EC) of the liquid with higher values indicating an elevated TDS level.

An in-stream limit of 300 µS/cm has been suggested by the U.S. EPA report EPA/600/R-10/023F to protect 95% of sensitive genera, primarily Ephemeroptera in the Central Appalachian region, whereas Cormier et al. (2011) recommended a level of 500 µS/cm to prevent the substantial disturbance of aquatic life. To meet the EPA conductivity limit for water, identifying potentially high conductivity producing materials in mine soil overburden and mine and coal processing waste streams followed by isolation or encapsulation have been suggested to be promising operational methods (Yeheyis et al., 2009; Rezaee et al., 2013). Given the vast number of mineral sources contained within typical mine and processing wastes, a quick and inexpensive method for providing an initial ranking of the potential leachability is needed. The measurement of the water conductivity resulting from the contact with the solid waste meets the requirements assuming acceptable accuracy and precision. Using the conductivity test as a screening mechanism, the waste materials that have the greatest potential for environmental harm can be identified and tested in more details using established static and kinetic leaching tests (Sobek et al., 1978, O'Shay etal., 1990; Kleinmann, 2000; Chotpantarat, 2011; Parbhakar and Lottermoser, 2015).

Acid base accounting (ABA) and neutralization potential (NP) tests are static tests that have been widely used for overburden characterization and acid mine drainage prediction. However, these tests do not predict the post-reclamation water quality where the NP is approximately equal to the maximum potential acidity (MPA). Kinetic tests are required for such an evaluation (Bradham and Caruccio, 1990).

Humidity cells, leaching columns, soxhlet reactors, shake flasks, pilot and large field leaching tanks are various types of apparati used for kinetic tests (ASTM D5744, Danielle, 2013; Sobek et al., 1982; Renton et al., 1988; Bruynesteyn and Hackl, 1984; Ziemkiewicz, 2013; Renton et al., 1984). The factors to be considered in kinetic leaching tests include: particle size (Brady, 1974; Horowitz et al., 1987; Bradham and Caruccio, 1990 and 1995), antecedent storage conditions (Caruccio and Geidel, 1981; Bradham and Caruccio, 1995), interleach storage conditions (Borek, 1994; Bradham and Caruccio, 1995), degree of saturation (Kleinmann, 2000; Watzalf, 1992), size, shape and structure of apparatus (Hornberger, 1998), volume and placement of samples in the test apparatus (Kleinmann, 2000), leaching interval (Gidel, 1979; Bradham and Caruccio, 1995), influent composition (Carrucio et al., 1981), rock-to-water ratio (Kleinmann, 2000), pore gas composition (Watzlaf, 1992; Cravotta et al., 1994; Guo et al., 1994), bacterial effects (Silverman, 1967; Kleinmann et al., 1981), pyrite morphology and texture (Caruccio and Parizek, 1968; Morrison, 1988; Borek, 1994) and carbonate content (Moses and Herman, 1991; Ziemkiewicz et al., 1995, Huggins et al., 2012). The kinetic leaching tests are usually expensive and time consuming and require performance under stringent laboratory conditions.

To quickly assess and compare leachate geochemistry from historical metal mine dumps, Hageman (2000) developed the USGS Field Leach Test (FLT). In this test, 1,000 mL of deionized water is slowly added to 50 g of prepared sample (20:1 water/solid ratio) in a wide-mouth plastic bottle. The capped bottle is vigorously hand shaken for 5 minutes and the contents allowed to settle for 10 minutes. The leachate is extracted from the bottle and analyzed for pH, specific conductance, alkalinity or other water quality characteristics. This test was later modified by Warner et al. (2013) for screening-level specific conductivity of drill core strata in the field or laboratory. Modifications to this method, as compared with FLT, were a reduction from 1,000 mL to 450 mL of either distilled or deionized (alternative methods) water with or without the addition of 50 mL hydrogen peroxide added to a 25 mg of sample (20:1 liquid/solid ratio) in a 1L wide-mouth plastic bottle. Hydrogen peroxide and other oxidants such as dissolved oxygen, Fe (III) ions, $KMnO_4$, and MnO_2 increase the oxidation rate of minerals especially pyrite and dissolution of the elements into the solution. As a result, an expedited assessment of the leaching potential for mineral types and individual fractions of the mine and processing waste can be achieved through the measurement of specific conductivity, and visual observation of effervescences. (Holmes and Crundwell, 2000; Schoonen et al., 2010; Warner, 2013, Lara et al., 2015).

As indicated in the above discussion, previous research has found that parameters such as particle size and volume along with leachate volume are impactful parameters in assessing leachability using kinetic leaching experiments. These parameters are directly linked to the exposure of the leachant to particle surface area. However, the FLT and the modified FLT do not specify a particle size distribution. As such, the ratio of exposed surface area (SA) to the liquid volume is not held constant and, in fact, reaches values greater than 25:1 which results in dilution of the ionic concentration thereby limiting the ability to provide an initial leaching potential assessment using electrical conductivity measurements. In addition, high liquid-to-solid ratio may limit predicting leaching characteristics of different materials exposed to various environmental conditions. Furthermore, the amount of oxidant (H_2O_2) added to the solution was not specified based on the mineralogical composition.

Electrochemical reaction steps controlling the dissolution rates of minerals occur at the mineral-solution interface. Therefore, the water volume to solid volume, weight or surface area is critical in leachate characteristics. Differences in volume-to-surface area ratio (VSAR) have resulted in a wide variation within empirical rate laws developed by researchers for minerals dissolution (Lollar, 2005). If this ratio is much greater than that occurring in the mine environment, the leachate will be diluted, resulting in lower concentration of TDS and conductivity of the leachate. This fact limits the application of the methods to predict the quality of water driven from waste streams as well as conducting conductivity screening-level tests. Patricio et al. (2015) found that the USGS leach test would underestimate conductivity released from coal mine water (Hornbeger, 1998; Kleinmann, 2000). Despite being of utmost importance, the effects of VSAR in determining leachate quality has not yet been studied in detail.

Previous investigations found that acid production rate, release rate of neutralization potential and production rate as well as total loads of ions such as sulfate, calcium, iron and manganese from minerals into solution varies in different size fractions and specific surface area (Pugh et al., 1984; Sasaki, 1994; Bradham and Caruccio, 1995; Nordstrom and Southam, 1997; Kleinmann, 2000; Chirita, 2003; Lollar, 2005). However, this conclusion was derived from the results obtained as a function of particle size using standard test procedures. Thus, the conclusion could be simply due to the variation in the VSAR rather than an increase in the surface area.

To develop a more meaningful standard test for rapidly performing conductivity screening-level assessments, the effects of three parameters and parameter interaction were evaluated using a statistically-designed test program which included 1) surface area (as quantified by material particle size, density, and mineralogy of the sample), 2) volume-to-surface area ratio (VSAR) and 3) the amount of oxidant on the leaching characteristics of a material . The selected response variable was specific conductance. The results of the parametric study was used to develop a standard procedure for a conductivity screening-level test. This modified test may be used for evaluation and comparison of leaching characteristics of different materials such as mine soils, waste streams of the coal and mineral processing plants or industrial wastes. The procedure can be used to screen the various materials at an operating mine and processing complex to identify materials that need to be further studied for potential isolation using long term column leaching experiments.

2.2 Materials and Methods

2.2.1 Sample collection and characterization

A representative sample of a coarse refuse stream from a coal processing plant treating Indiana 5-B central coal seam was collected. Coal from this source is characterized as high-volatile 'C' bituminous coal with high concentrations of organic and pyritic sulfur. Upon receiving the sample, the material was crushed using laboratory jaw crusher to achieve a top size of 6.35 mm, which was selected based on the leaching test standard described by the D-5744 ASTM procedure. After crushing, the sample was split into 1 kg sample lots using a Jones riffler. The samples were placed into plastic container and stored until needed in the test program.

Characterization of the coarse refuse was conducted on a representative 1 kg sample lot. As shown in Table 2.1, proximate, ultimate and sulfur forms analysis results found that the sample contained 54.5 % ash-bearing material and the sulfur was primarily in the form of pyritic sulfur from which the oxidization product generates acidic runoff. The minerals present within the ash-forming material were identified and their content quantified using X-ray Diffraction (XRD) by the Rietveld method. The mineral was mostly pyrite at 43% followed by nearly equal amounts of quartz, illite and kaolinite. A minor amount of calcite was also present which has value as a neutralizing component to counter the acid generators. These findings were confirmed by results obtained from X-ray fluorescence (XRF) analysis of the ash produced by combusting the coarse refuse sample at 500 ^oC. The ash was primarily comprised of iron oxide which mostly resulted from the combustion of pyrite. Significant quantities of aluminum and silica oxides were found as expect from the XRD results. The low CaO concentration indicated limited natural buffering capacity.

Table 2.1. Sample Characterization.

Ultimate analysis (%)		Forms of Sulfur (%)		Mineral (%)*		%Oxide (ash basis)**			
Ash	54.5	Total S	29.3	Pyrite	43	Al_2O_3	10.41	K2O	1.38
Moisture	1.6	Sulfate	1.1	Quartz	20	BaO	0.02	SiO2	24.41
C	17.9	Organic	7.6	Illite	19	CaO	0.45	Na2O	0.24
H	1.6	Pyritic	20.7	Kaolinite	18	Fe_2O_3	61.48	SrO	0.02
N	0.04			Calcite	<5	MgO	0.58	SO3	0.45
O	<0.01					P_2O5	0.15	TiO2	0.43

* As %wt of mineral matter, **Major element analyses (ash basis) of 500˚C ash prepared from the sample

Prior to performing a modified conductivity screening test, a 1 kg sample was screened using sieves having 1 mm and 0.15 mm apertures which resulted in three particle size fractions: i.e., coarse (6.35 x 1 mm), fine (1 x 0.15 mm) and ultrafine (minus 0.15 mm). The ultrafine fraction was not used in the screening test and thus was discarded. The coarse and fine size fractions were subjected to float-and-sink analysis at a specific gravity of 2.95 using a lithium metatungstate (LMT) solution. In this process, the particle size fraction is submerged into an LMT medium contained in a 2-liter beaker followed by removal of the float fraction using a screening tool which allowed the excess medium to drain. The remaining medium was filtered to recover the particles that settled to the bottom of the beaker. Both the float and sink fractions were rinsed and dried. As a result, four particle sized and density fractionated samples were produced as shown in Table 2.2 which were used for the modified FLT parametric study. These particle size and density fractions can be readily recovered through normal processing plant operations if isolation is required for any of the fractions due to acid generation and the release of trace elements that are harmful to the environment.

Table 2.2. Four sized and density fractionated samples.

Size Distribution	2.95 Float	2.95 Sink
6.35 x 1 mm	Coarse-Float (CF)	Coarse-Sink (CS)
1 x 0.15 mm	Fine-Float (FF)	Fine-Sink (FS)

Leaching characteristics of the sample were studied by conducting two long-term dynamic column leaching tests, which were performed according to standard ASTM method D-5744, and static leaching tests. The two long-term leaching test was utilized to simulate various storage conditions associated with typical coal waste disposal practices. The static test was designed to simulate the stable storage of coarse waste materials submerged under water that are used for embankment construction of impoundments. The dynamic test was designed to model storage under more variable conditions similar to those of coarse refuse piles that provide intermittent exposure to air and variations in humidity.

2.2.2 Conductivity Screening Test

As described in a previous section, the conductivity screening tests were conducted in accordance to the modified procedure described by Warner et al. (2013) with the exception of the variable quantities being studied in the investigation including particle size and density, solid mass and the volumetric amount of distilled water and oxidant. In each experiment, a specified amount of solid sample was added to a volume of distilled water and oxidant in an appropriately sized container whose volume varied due to the evaluation of leachate volume-to-particle surface area ratio effects. The contents were mixed using a mechanical vibration device for a period of 15 minutes. After allowing 5 minutes for the sediments to settle, the conductivity and pH of the leachate were measured and recorded.

2.2.3 Parametric Study

To quantify the importance of surface area and the interactive effects with particle size, a three-level statistically designed program was conducted which included several repeat tests to assess experimental error. Given that the effects may vary with mineralogy, a separate experimental program was conducted on two particle size fractions and two density fractions as indicated in Table 2.2. A three-level test program based on the Box-Behnken statistical design was performed to evaluate the effects of surface area (SA), leachant volume-to-surface area ratio (VSAR) and amount of oxidant on the conductivity of samples. The range of parameter values evaluated are shown in Table 2.3. The 20 to 80 cm^2 value range for surface area is a typical for coarse refuse material in the coarse waste streams. The volume-to-surface area ratio (VSAR) used in the original conductivity test is 25 cm^3/cm^2 whereas the typical leaching column experiment utilizes a ratio of 1 cm^3/cm^2. The highest VSAR value was established to meet the symmetrical requirements of a three-level test design. The oxidant range was established based on a typical value of 15% and a general lack of quantitative data on the impact on conductivity.

Table 2.3. Parameter value ranges investigated in the Box–Behnken test program.

Parameter	Level		
	Low	Medium	High
SA (cm^2)	20	50	80
VSAR (cm^3/cm^2)	1	25.5	50
Oxidant (%)	0	15	30

Surface area (SA) was calculated using the following expression:

$$SA = 6f\frac{m}{\rho\sqrt{(x_1 \times x_2)}} \tag{2.1}$$

in which, SA is the surface area (cm^2); m the weight of the material (g); ρ the solid density of the material (g/cm^3); $\sqrt{(x_1 \times x_2)}$ the geometric mean diameter of the material (cm); x_1 and x_2 bottom size and top size (cm) of the sample determined by sieve analysis; and f the shape factor, which is a function of the type and shape of the materials.

For example, a shape factor of 1 and 1.24 may be used for approximately spherical fly ash and cubic lime stone dust particles, respectively. For irregularly-shaped hydrated lime, a higher shape factor should be used. The values of shape factor for different types of materials ranges from 1 to 2, as shown in Table 2.4 (Ishai and Craus, 1977). A shape factor of 1.5 was applied for the studied material since their shapes are neither completely irregular nor cubic.

Table 2.4. Particle shape factors for different materials used for the determination of surface area.

Material	Shape factor (f)
Fly ash	1
Limestone	1.24
Hydrated lime	2
Glass beads	1
Dolomite	1.24
Basalt	1.24

After calculation of equivalent mass of particles corresponding to the pre-determined SA, the required volume of deionized water to achieve the VSAR was added to the solids in a capped container. The samples were shaken for 15 min using a mechanical shaker, and the conductivity of the leachates were measured. For 3 parameter evaluation, 12 tests with an additional 5 repeat tests at the central parameter values were conducted for each sample. A total number of 68 tests were conducted (Box and Draper, 1987; Montgomery, 2001; Myers and Montgomery, 2002).

2.3 Results and Discussion

2.3.1 Leaching Characterization

The leaching characteristics of the coarse reject and the corresponding leachate conductivity were evaluated using static and dynamic column leach tests. As shown in Figure 2.1, the supernatant liquid pH was strongly acidic during the initial period of both the dynamic and static tests and remained acidic throughout the entirety of the tests. The lower acidic condition in the dynamic column leaching test was due to the more aggressive oxidation as a result of weekly cycles of alternating periods of dry air (3 days), humid air (3 days), followed by leaching using de-ionized water on the seventh day. High pyrite content and a negligible amount of buffering capability (calcite content) in the sample was the primary reason for the strong acidic medium when the sample was contacted with water.

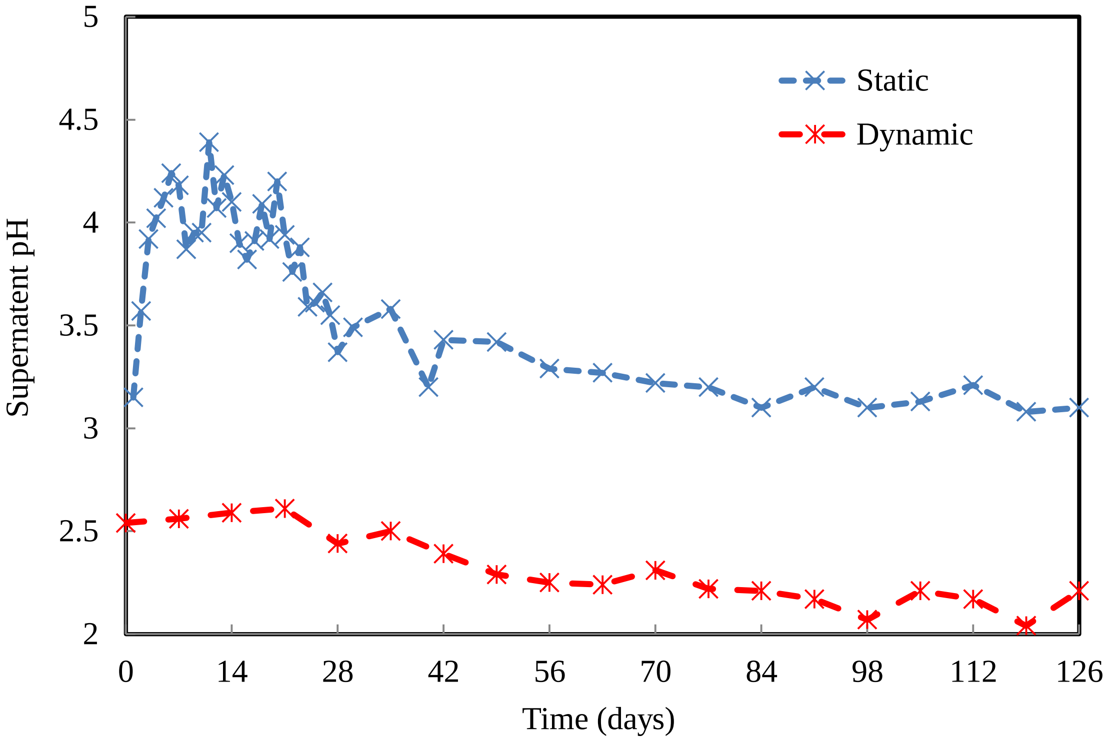


Figure 2.1. Variation of supernatant liquid pH as a function of time in static and dynamic leaching tests.

Under these acidic conditions, a high amount of trace elements were released into the solution (Figure 2.2), thereby increasing the conductivity level of the leachate. The electrical conductivity (EC) of the supernatant liquid collected from the dynamic column leach tests was measured periodically throughout the duration of the tests. As shown in Figure 3.2, the EC value trended downward after an initial high reading throughout the test period varying from around 6000 µS/cm to over 14000 µS/cm. The conductivity of the leachate solution collected at the end of the static leaching test was also measured and the value of 7,440 µS/cm agrees well with less aggressive conditions in the static test.

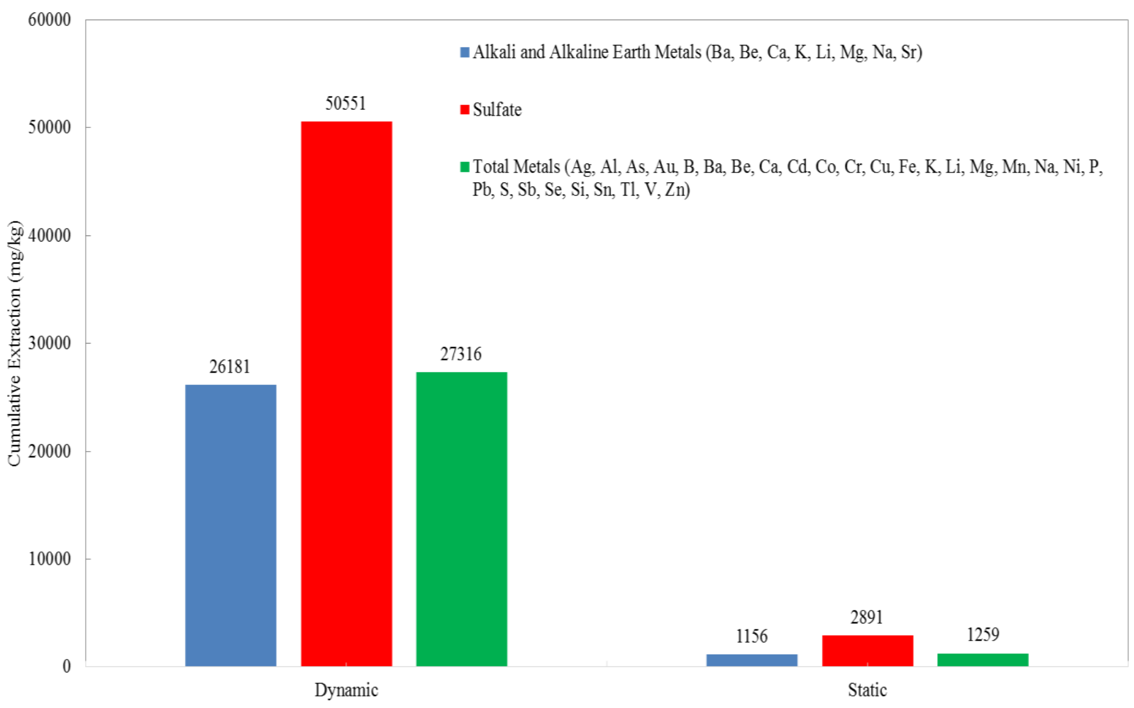


Figure 2.2. Cumulative extraction of alkali and alkaline earth elements, sulfate and total metals from unit weight (kg) of the coarse refuse sample in dynamic and static leaching tests.

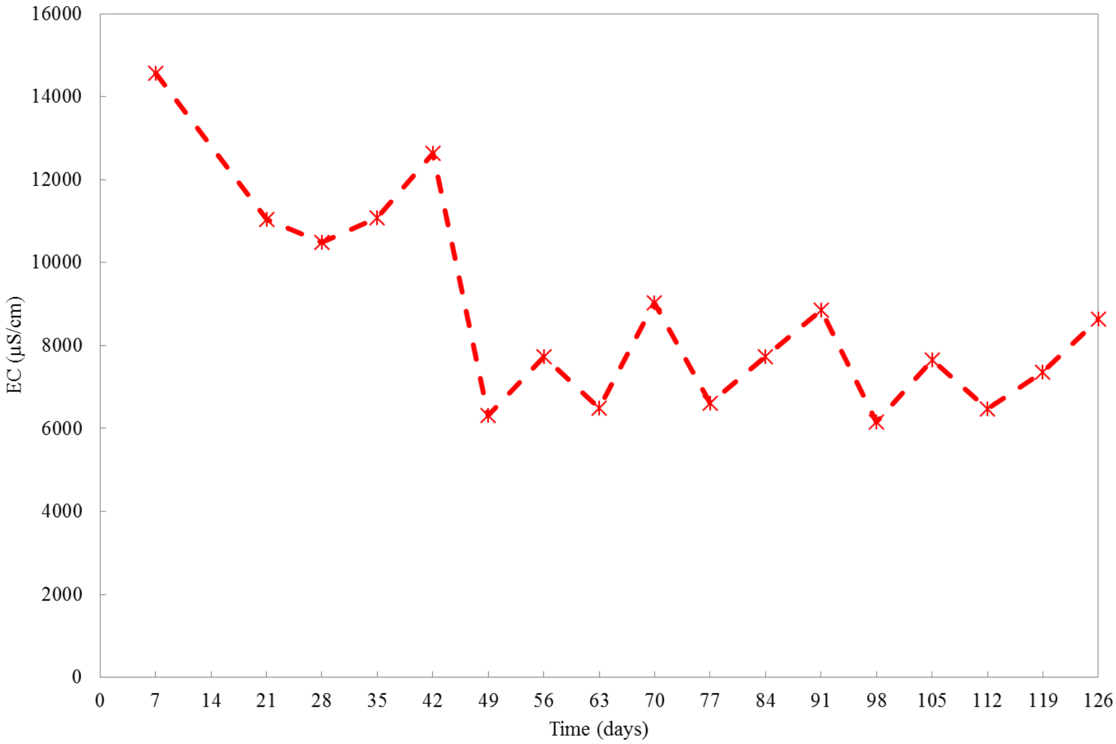


Figure 2.3. Conductivity of the supernatant liquid measured as a function of time in the dynamic leaching test for the non-segregated coarse refuse material.

2.3.2 Statistical Evaluations of Conductivity Populations

Experimental programs conducted according to a Box-Behnken statistical design was performed on four samples having different particle size and density to evaluate the independent and interactive effects of particle surface area (SA), leachant volume-to-surface area ratio (VSAR), and the amount of oxidant on the electrical conductivity (EC) of supernatant liquid. The results were used to develop a standard procedure for conductivity screening-level testing.

The test conditions and the EC values from the 68 conductivity screening level tests are provided in Table 2.5. Seventeen tests were conducted on each of the four samples, i.e.,: fine-float, fine-sink, coarse-float and coarse-sink. EC values varied from 1 to 3,530 µS/cm and the variation was the greatest for the coarse-sink material which likely contained the highest amount of pyrite.

Table 2.5. Summary of independent parameters and measured values for the response variable.

Trial Order	Parameters			Response Variables: EC (µS/cm)			
	S.A. (cm^2)	Vol.: S.A. (cm^3:cm^2)	Oxidant (%)	Fine-Float	Fine-Sink	Coarse-Float	Coarse-Sink
1	20	25.5	30	79	170	164	608
2	50	1	30	722	1,414	1,106	3,530
3	50	25.5	15	37	87	72	406
4	80	25.5	0	2	6	17	24
5	50	25.5	15	38	98	90	363
6	50	25.5	15	40	61	52	447
7	80	50	15	27	55	39	184
8	80	1	15	487	828	643	1,528
9	20	25.5	0	3	6	24	387
10	50	25.5	15	33	62	88	446
11	80	25.5	30	73	247	100	813
12	50	50	30	48	160	134	358
13	50	25.5	15	34	65	45	434
14	20	50	15	29	59	110	278
15	50	1	0	63	92	360	3,450
16	20	1	15	653	505	743	3,480
17	50	50	0	1	4	6	205
Average (Standard Error)				139 (13)	231 (22)	223 (18)	997 (72)

The initial statistical analysis focused on an assessment to determine if there are statistically differences in the population means using a one-way analysis of variance (ANOVA). The null hypothesis was that all population means were equal and the alternative hypothesis was that at least one mean was different. Based on a comparison between the F-statistic value of 6.07 and the value corresponding to a confidence interval level of 95%, the null hypothesis was rejected which meant that at least one of the population mean values was statistically different from the other three. This was the first indication that particle size and density have an impact on the EC values resulting from oxidation and contact with water.

As a result, a statistical analysis was conducted to determine which group or groups among the four data sets have different population means. The analysis individually compared the mean of each population with each of the means of the other three populations. The null hypotheses in each case was that the pair of means were equal. The only rejected hypotheses were the equality of the means associated with the coarse-sink fraction with the means of other fractions as shown in Table 2.6. Given the specific gravity for pyrite of 4.8 relative to 2.9 or lower for most of the other minerals, the finding that the mean associated with the coarse-sink was different than the other samples was understandable. The high conductivity level of this fraction is primarily due to the high amount of pyrite along with unliberated lighter minerals such as clay minerals in this fraction. Although clay minerals are expected to be presented in the float fractions, they may not be effectively separated in density fractionation of coarse materials due to lack of complete liberation. As a result, oxidation of pyrite not only generates an acidic condition which releases associated calcophilic trace elements, but also dissolves lithophilic trace elements associated with the other mineral content in that fraction.

Table 2.6. T-tests' results for testing the equality of pairs of the means.

Null Hypothesis	Alpha Value	Decision
μ fine-float = μ fine-sink	7.69E-02	Not Reject
μ fine-float = μ coarse-float	2.60E-01	Not Reject
μ fine-float = μ coarse-sink	2.33E-08	Reject
μ fine-sink = μ coarse-float	5.07E-01	Not Reject
μ fine-sink = μ coarse-sink	1.69E-05	Reject
μ coarse-float = μ coarse-sink	1.60E-06	Reject

This finding demonstrates the ability of the applied experimental approach to recognize differences in conductivity level and identifying the fraction within a given waste stream that needs to be isolated to prevent negative impacts on the environment.

2.3.3 Parametric Evaluation

In an effort to evaluate the parameter and parameter interactive effects, empirical models were developed which were used to predict the electrical conductivity (EC) resulting from a combination of surface area (SA), volume-to-surface area ratio (VSAR) and oxidant addition values. Linear, quadratic and cubic models were considered. Linear models were found to provide statistically poor predictions for all four data sets while the cubic model significantly reduced the degrees of freedom and thus was considered unfavorable. The p-values obtained from ANOVA for quadratic models were less than 0.05 for four data sets, which is indicative that the models are significant (Table 2.7). As such, the following statistical evaluations were conducted using quadratic models for the four data sets.

The ability of models to accurately estimate the response variable (y_i) was measured by the coefficient of determination (R^2) as calculated by the expression:

$$R^2 = 1 - \frac{\sum (y_i - \hat{y}_i)^2}{\sum (y_i - \bar{y}_i)^2} \tag{2.1}$$

where y_i is the electrical conductivity measured during a given test, $\hat{y}$ the predicted conductivity value and $\bar{y}$ the mean value obtained from an experimental data set. The quadratic models for all the four samples were found to accurately predict the conductivity values as indicated by R^2 values greater than 0.9.

To ensure that each model was not constrained by a low degree of freedom, the adjusted coefficient of determination (R^2_{adj}) was quantified for each data set using the following equation:

$$R^2_{adj} = 1 - \frac{n-1}{n-(k+1)}\left(1 - R^2\right) \tag{2.2}$$

where n and k are the number of data points and parameters, respectively. As implied from Eq. 3.3., R^2_{adj} must always be less than R^2, and their difference is indicative of an excessive number of parameters used in the modes. The differences were less than 0.033 for all of the four models derived in this study thereby meeting the required standards to accepted

After acceptance of the models, the parametric and parameter interaction terms in each model were evaluated for their statistical significance. The null hypothesis used for the assessment was that the corresponding coefficient value was zero. Table 2.7 summarizes the test statistic values which represent the probability that the parameters or their associated interactions has no effect on the response variable. A prescreening of the parameters and interactions was conducted through rejection of any term having a t-value greater than 0.05 with exception of hierarchy conditions. The models were then modified according to the rejected terms. Table 2.7 provides the t-values for the remaining model terms established for each of the four data sets.

Table 2.7. Statistical significance of the parameters and parameter interactions and fit analysis for the four quadratic models.

Quadratic models for estimating EC in the samples							
Fine-Float		Fine-Sink		Coarse-Float		Coarse-Sink	
Parameter	t-statistic	Parameter	t-statistic	Parameter	t-statistic	Parameter	t-statistic
Quadratic Model	5E-06	Quadratic Model	5E-06	Quadratic Model	3.79E-08	Quadratic Model	1.02E-06
B-VSAR	5.8E-06	B-VSAR	1.8E-05	B-VSAR	3.96E-08	A-SA	0.065861
C-Oxidant	0.00368	C-Oxidant	0.0003	C-Oxidant	0.000213	B-VSAR	3.34E-07
BC	0.00341	BC	0.00087	BC	0.001311	AB	0.032758
B^2	0.00019	B^2	0.00054	B^2	1.28E-06	B^2	3.61E-05
R-Squared	0.90395	R-Squared	0.90412	R-Squared	0.957842	R-Squared	0.926695
Adj R-Squared	0.87193	Adj R-Squared	0.87217	Adj R-Squared	0.94379	Adj R-Squared	0.90226

An observation of the significant model terms in Table 2.7 reveals that the most significant parameter effecting the leachate EC value is VSAR for all four materials while SA has no independent effect on conductivity. Figure 2.4 also confirms that EC is a function of VSAR to the second order, and increasing the VSAR decreases the EC significantly due to dilution. The graphs in Figure 3.3 were plotted at constant values SA and oxidant values of 50 cm^2 and 30%, respectively. However, the trends were independent of these values.

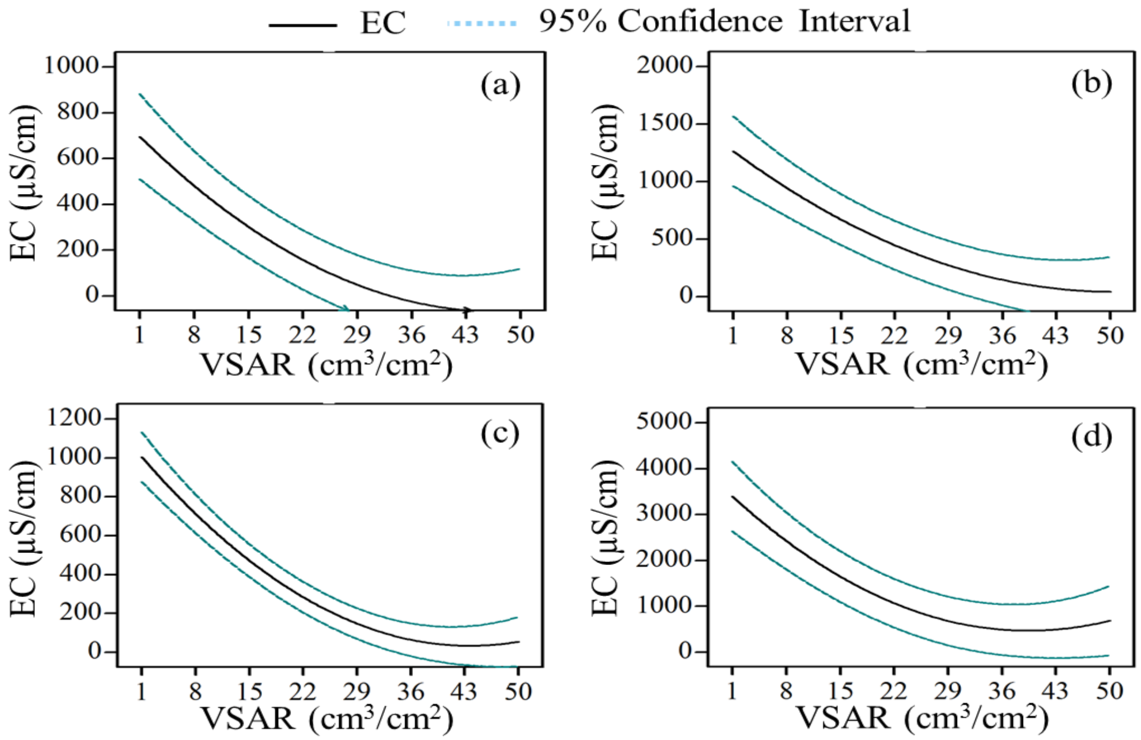


Figure 2.4. Relations between EC and VSAR for different size-density fractionated samples: (a) Fine-Flat, (b) Fine-Sink, (c) Coarse-Float, (d) Coarse-Sink.

Figure 2.5 shows the effect of SA on EC for all samples along with 95% confidence interval (CI) bands using VSAR and oxidant values of 25.5 and 30%, respectively. Evaluations at different VSAR and oxidant values indicated that the trends were independent of VSAR and oxidant percentage. The graphs confirmed that EC is independent of SA. This finding is due to the fact that EC is caused by the mitigation of ions to the aqueous phase after the dissolution of minerals, and the chemical reaction occurs at the mineral-solution interface. As well-known from previous studies and in practice, leaching is a function of the ratio of particle surface area to the leachant volume (van der Sloot, et al. 1997; Lolar, 2005).

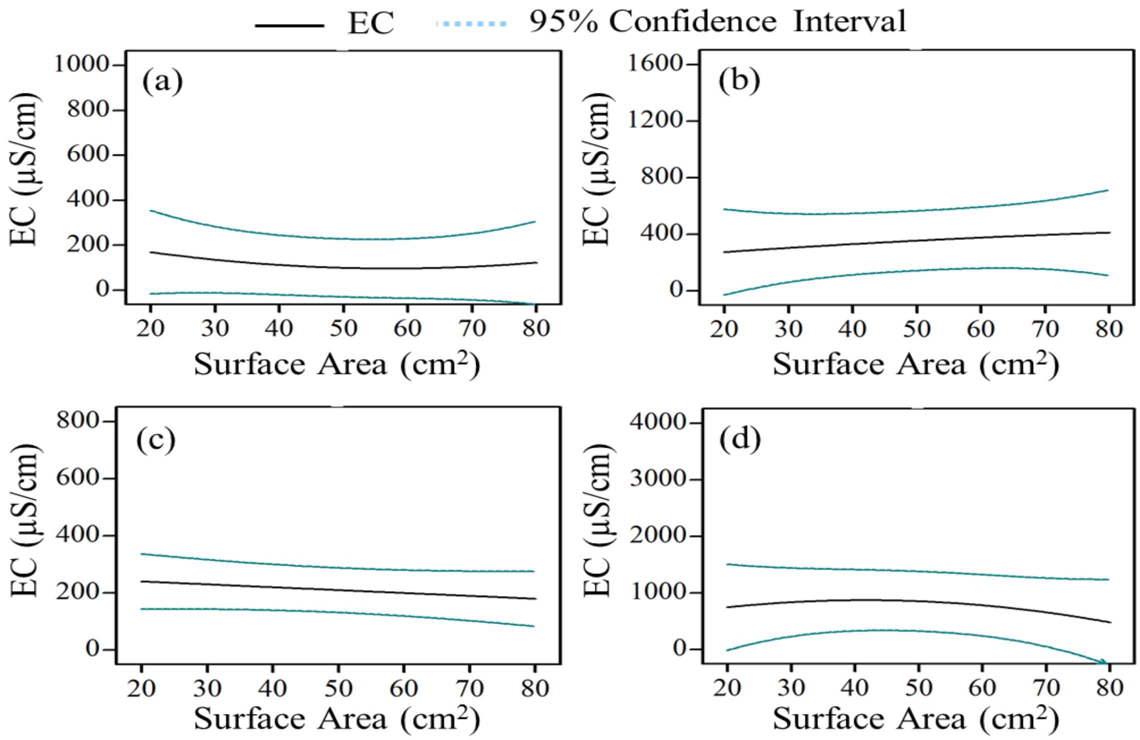


Figure 2.5. Relations between EC and SA for different size-density fractionated samples: (a) Fine-Flat, (b) Fine-Sink, (c) Coarse-Float, (d) Coarse-Sink.

The next most significant parameters in the models with the exception of the coarse-refuse fraction were the oxidant percentage and its interaction with the VSAR. Figure 2.6 confirms the predicted significance of the percent of oxidant on three of the four materials with the exception of the coarse-sink fraction. It is noted that the conductivity of the leachate from coarse-sink is already significantly high relative to the other materials. As described by the models and the graphs in Figure 2.6, the variation of EC with percent of oxidant is linear for all materials except the coarse-sink fraction. The trends were independent of the selected other parameter values (VSAR:1 cm^3/cm^2 and SA:50 cm^2)

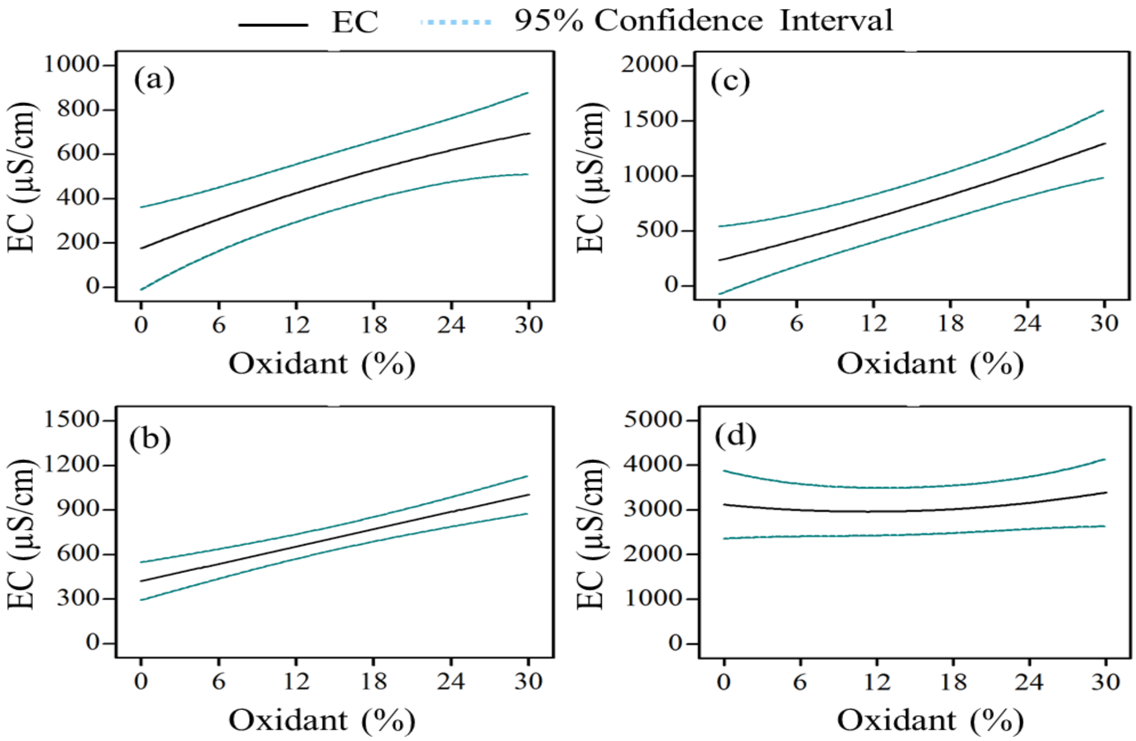


Figure 2.6. Relations between EC and oxidant for different size-density fractionated samples: (a) Fine-Flat, (b) Fine-Sink, (c) Coarse-Float, (d) Coarse-Sink.

As noted, the interaction between the percent of oxidant and VSAR is significant and the impact on EC is shown in Figure 2.7. As shown, VSAR has a significantly greater impact than the amount of oxidant on EC. Depending on the sample mineralogy and TDS value after a given dilution ratio, the EC of the supernatant water significantly decreases. This observation is consistent with the dependency of EC with the second order of VSAR in the developed quadratic models.

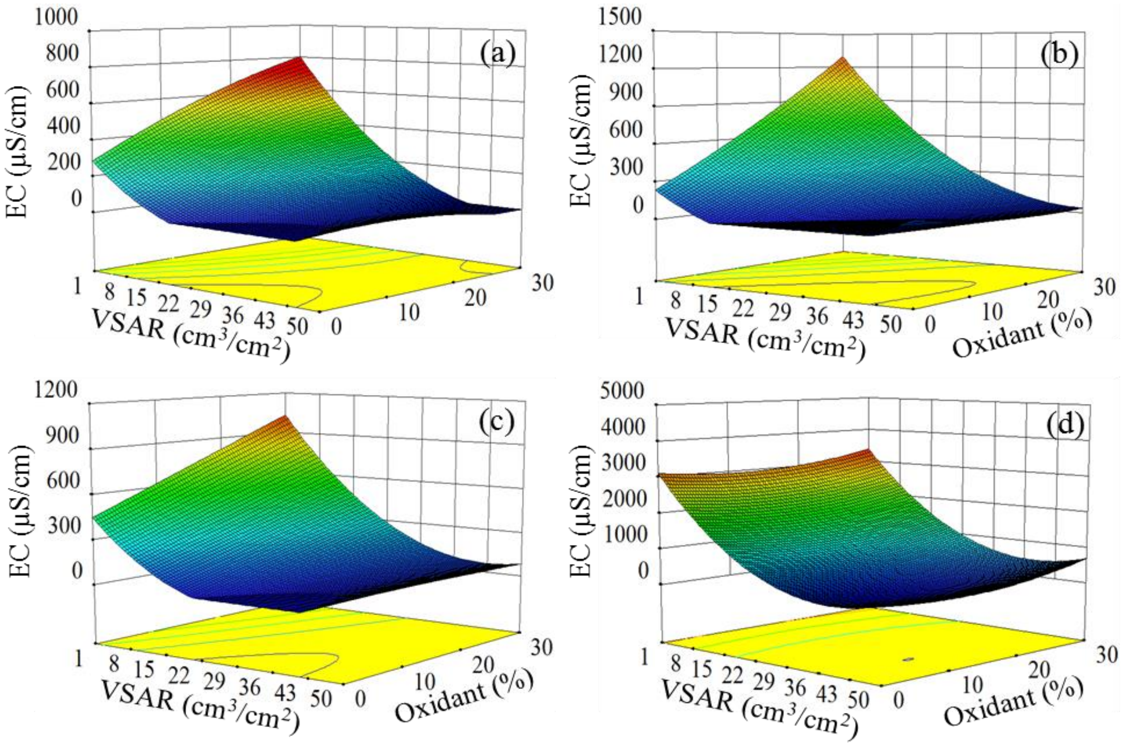


Figure 2.7. Predicted interactive effects of VSAR and oxidant on EC for different size-density fractionated samples: (a) Fine-Flat, (b) Fine-Sink, (c) Coarse-Float, (d) Coarse-Sink

An additional observation from Figure 2.7 is that a 1:1 VSAR ratio for all four fractions results in an elevated conductivity level without the use of an oxidant, which simplifies the conductivity screening-level test. As a result, one may consider just using a 1:1 VSAR in the conductivity screening-level test and eliminate using the oxidant since hydrogen peroxide is not naturally available during dissolution of minerals in a mining environment. This 1:1 VSAR value is also more representative of the mining environment, and is also commonly used in soil testing as suggested by a number of researchers for implementation in leaching columns and weathering cells (Kleinmann, 2000).

2.3.4 Modified Conductivity Test Procedure

Understanding the effect of the parameters facilitates modification of the previous conductivity screening-level tests. Based on the parametric analysis, it is recommended to modify the standard conductivity test procedure as illustrated in Figure 2.8 and described as follows:

1- Particle size analysis of a representative sample by sieving to determine the top and bottom size of the material.
2- Measure solid density
3- Calculate surface area using Eq. 3.1.
4- Add distilled water to the sample at a volume that provides a volume to surface area ratio (VSAR) of 1:1.
5- Shake the capped container for 15 min.
6- Measure conductivity of the leachate after allowing particles time to settle. The leachate may be filtered for further analyses.

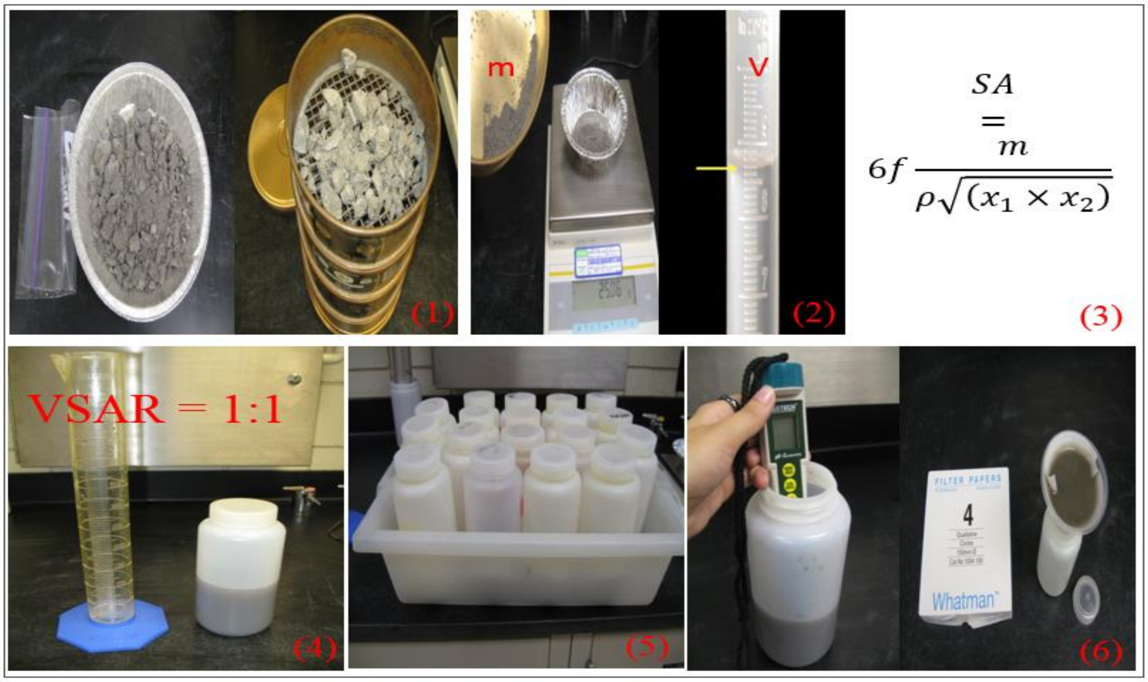


Figure 2.8. Schematic of the modified conductivity screening-level procedural steps including the determination of surface area.

2.4 Conclusions

Dissolution of the mineral content comprised in processing waste streams results in the release of major and trace elements thereby causing an elevation of conductivity of the water in contact with the materials**.** Identification and separation followed by isolation/encapsulation of the fractions causing the elevation of TDS and conductivity of water may minimize the environmental effects of waste disposals. To achieve this goal, an accurate conductivity screening-level test that can provide a timely assessment of the various components in a waste stream is needed.

Understanding the effect that the various parameters have on the conductivity of the water in contact with the solid surfaces is necessary for developing an adequate conductivity test.

Particle surface area, liquid volume-to-surface area ratio and the amount of oxidant were identified as key parameters impacting electrical conductivity of the leachate. The effects of each parameters were quantified using data obtained from a test program that was conducted based on a statistical three-level design known as the Box-Behnken method. Separate test programs were conducted on two different particle size fractions and density fractions from a coarse coal waste material which effectively varied the mineralogical composition. A statistical analysis of the test results indicated that the coarse and high density fraction provided supernatant liquid conductivity values that were significantly different than those obtained from the coarse, low density material and the high and low density fractions of the small particle size fraction. This finding is likely due to the high pyrite content in the heavy fraction and low concentration of minerals like calcite that could provide neutralizing potential.

Quadratic models were developed using the parametric test results which provided an accurate means to quantify electrical conductivity as a function of the parametric values and their associated parameter interactions. Based on a statistical analysis of the models, the significance of the parameter and parameter interactions followed the order of 1) liquid volume-to-solid surface area ratio (VSAR), 2) oxidant amount through the interaction with VSAR, and 3) interaction between VSAR and surface area. Surface area was not found to be an independently significant parameter for all four material cases. A low VSAR value of 1:1 produced an elevated supernatant conductivity value in all cases and thus points to an acceptable standard for a modified conductivity screening test procedure.

Based on the findings of the parametric study and subsequent statistical analyses, a modification to the existing standard conductivity screening test was developed which consists of the following steps: 1) conduct a particle size analysis of the material by sieving to determine top size and bottom size for calculation of the geometric mean diameter, 2) measure density of the solids 3) calculate particle surface area calculation, 4) add a quantity of distilled water to the sample in a container that will meet a 1:1 ratio of liquid volume-to-particle surface area, 5) agitate the capped container for 15 minutes and 6) measure the conductivity of the supernatant after allowing time for particles to settle. This procedure can be applied for conductivity screening-level of various waste streams.

3. ELECTRICAL CONDUCTIVITY SCREENING FOR DEVELOPING COAL PROCESSING WASTE DISPOSAL STRATEGIES

Summary: An environmental concern at coal processing operations is the release of elements resulting from the oxidation or dissolution of certain minerals contained in the process waste streams. Using a standard conductivity test, the electrical conductivity (EC) of the water samples obtained from mixing with various particle size and density fractions of a given plant waste material were measured as an indicator of total dissolved solids. As a result, the particle size and density fractions contributing to high EC levels were identified with the objective of potentially extracting the identified fractions and isolating the material to reduce the potential for negative environmental impacts. The results showed that the EC generated from coarse refuse streams were significantly higher than the values obtained from fine refuse streams. Crushing the coarse samples to a finer particle top size showed potential for reducing the EC of the supernatant water, at least in the short term, due to the liberation of certain minerals, such as calcite, which provide enhanced buffering capability. Furthermore, the high specific gravity (>2.68) fractions were found to be the primary source of elevated EC levels. The remaining fractions were found to be of minimal environmental concern. Mass balancing of the coal processing plant streams indicated that the high density fractions comprised less than 10% of the coal waste streams. Liberation and separation followed by the isolation of this fraction significantly minimizes the negative environmental impacts associated with the handling and placement of coal refuse materials.

3.1 Introduction

Modern coal preparation facilities incorporate a wide array of low-cost solid-solid and solid-liquid separation processes for coal upgrading to improve utilization characteristics of the product coal. While these benefits are well documented, the coal industry often overlooks the opportunity to further integrate coal preparation as an environmental control system. In fact, coal processing facilities have long played a critical role in reducing the emissions of pollutants at coal-fired power stations.

Many of the air pollutant precursors are associated with the mineral matter commonly rejected by coal preparation plants. The mode of occurrence of trace elements in coal has been well studied by many researchers (Zubovic, 1966; Gluskopter et al., 1977; Finkelman, 1981; Clarke and Sloss, 1992; Querol et al., 1995; Wang et al., 2009; Vejahati et al, 2010, Huggins et al, 2012). The pre-combustion rejection of trace elements by coal preparation is attractive since the waste rock is relatively coarse and has a lower reactivity than the high-surface-area ash generated by power stations (Jacobsen et al., 1992). In-plant sampling campaigns conducted by various researchers (Luttrell et al., 2000) suggest a good correlation between the rejection of mineral matter and the removal of trace elements during physical cleaning. The data suggests that trace elements are typically rejected at levels of 40%-70% by weight using conventional preparation technologies.

The rejected mineral matter is commonly placed into surface storage areas which are refuse piles and impoundments in mountainous terrains or a ponding system in flat areas. Refuse piles are designed to store the coarse refuse materials which can be easily dewatered and hauled by trucks or conveyor belts. Due to recent changes in environmental rules, a few operations are employing the use of high pressure filters to dewater the fine refuse which allows co-disposal with the coarse refuse in a piling system. In most cases, impoundments are used to store the fine coal waste in slurry form with typical solid concentrations of around 30% by weight. A portion of the coarse coal waste is used to construct the embankment of the impoundment. The waste materials are exposed to ambient air and water which promotes the oxidation of minerals such as pyrite (FeS_2) and dissolution of associated elements. This process impacts the quality of the water that permeates through the impoundment and flows into downstream ponds as well as the discharged water from the coarse refuse piles.

Weathering of pyrite has the potential to create highly acidic leachate which degrades water quality by elevating metals and sulfate concentrations that exceed water quality standards (Moses, 1990; Nordstrom et al., 2000; Dold & Fontboté, 2001). Three major steps involved in pyrite oxidation include:

(1) Sulfur oxidation as described by:

$$\mathrm{FeS_2} + 7/2\ \mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{Fe^{2+}} + 2\,\mathrm{SO_4^{2-}} + 2\,\mathrm{H^+} \qquad (3.1)$$

In this initial step, pyrite is oxidized through adsorbing oxygen and water to its partly protonated surface by bonding to Fe^{2+}. Every mole of pyrite then produces one mole of ferrous iron (Fe^{2+}), two moles of sulfate (SO_4^{2-}), and two moles of H^+. In addition, chalcophilic and other associated elements are also released into the solution (Nordstrom et al., 1979; Nordstrom, 1982; Moses et al., 1987; Fornasiero et al., 1994; Ehrlich, 1996, Rezaee et al., 2013). Pyrite oxidation by ferric iron at pH below 3 is approximately 10 times faster than by oxygen (Ritchie, 1994; Dold, 2010) due to the more efficient electron transfer of Fe^{3+} (Luther, 1987).

(2) Ferrous iron oxidation according to the following reaction:

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \qquad (3.2)$$

The reaction produces ferric iron (Fe^{3+}) which is the primary oxidant, especially at low pH conditions based on the reaction:

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \qquad (3.3)$$

O_2 becomes the major oxidant under circumneutral pH due to the diminished solubility of Fe^{3+} (Singer and Stumm, 1970; Dold, 2010).

(3) Hydrolysis and precipitation of ferric complexes such as Fe(III) oxyhydroxide, which is the main acid producer reaction (Dold, 2010), i.e.,

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_{3(s)} + 3\ H^+ \qquad (3.4)$$

As a result, the overall reaction is a release of 4 moles of H^+ per mole of pyrite as indicated by:

$$\mathrm{FeS_2 + 15/4\ O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2\,SO_4^{2-} + 4\,H^+} \qquad (3.5)$$

Pyrite oxidation decreases by precipitation of the secondary Fe(III) hydroxides due to the coating effect which prevents the exposure of the pyrite to further oxidation (Blowes et al., 1991; Evangelou & Zhang, 1995; Dold et al., 2009). The overall reaction of pyrite oxidation facilitates the release of major and trace elements into the solution as a result of the elevated hydroxide solubility of metals in strong acidic conditions. As a result, the negative impact can be detected by high electrical conductivity values measured in the supernatant water that has interacted with the waste material.

Pyrite oxidation, acid generation, release of sulfate, iron and trace elements could be abated by the buffering capability provided by natural chemical or biological processes, such as carbonate mineral dissolution, release of exchangeable cations associated with the clay minerals (Toran, 1987; Nicholson et al., 1988; Blowes & Ptacek, 1994; Huggins et al., 2011) or bacterial sulfate reduction (Herlihy et al., 1988; Moses, 1990). For example, the formation of insoluble jarosite ($\mathrm{NaFe_3(SO_4)_2(OH)_6}$) and gypsum ($\mathrm{CaSO_4.2H_2O}$) through the release of sodium and calcium from the dissolution of carbonate minerals provides natural pH neutralization potential. The formation of these minerals is explained by the following reactions:

$$\mathrm{3\,FeS_2 + 3\,H_2O + 13.5\,O_2 + [Na^+]_{sol'n} \rightarrow NaFe_3(SO_4)_2(OH)_6 + 4[SO_4]^{2-}{}_{sol'n}} \qquad (3.6)$$

$$[\mathrm{Ca}^{2+}]_{\mathrm{sol'n}} + [\mathrm{SO}_4^{2-}] + 2\,\mathrm{H_2O} \rightarrow \mathrm{CaSO_4.2H_2O} \tag{3.7}$$

These reactions show the release of some sulfate to the leachate, the lack of iron mobilization, the absence of acid generation ($[\mathrm{H}^+]_{\mathrm{sol'n}}$), and the formation of jarosite and gypsum subject to the presence of a critical concentration of calcium and sodium ions. At or above the critical concentrations, the acidity is buffered to near neutral pH, and mobilization of iron and trace metals associated with pyrite would be minimized.

Waste materials with naturally high buffering capability may also provide elevated electrical conductivity values of the supernatant liquids due to increased solubility of metals in alkaline conditions. For example, the dissolution of carbonate minerals such as calcite, dolomite or magnesite will provide an environment that results in elevated electrical conductivity values as described by the following three parallel reactions which occur at the mineral/water interface: (Plummer et al., 1978; Chou et al., 1989; Wollast, 1990):

$$\mathrm{MeCO_3} + 2\mathrm{H}^+ \underset{\mathrm{k-1}}{\overset{\mathrm{k_1}}{\leftrightarrow}} \mathrm{Me}^{2+} + \mathrm{HCO_3^-} \tag{3.8}$$

$$\mathrm{MeCO_3} + \mathrm{H_2CO_3^*} \underset{\mathrm{k-2}}{\overset{\mathrm{k_2}}{\leftrightarrow}} \mathrm{Me}^{2+} + 2\mathrm{HCO_3^-} \tag{3.9}$$

$$\mathrm{MeCO_3} \underset{\mathrm{k-3}}{\overset{\mathrm{k_3}}{\leftrightarrow}} \mathrm{Me}^{2+} + \mathrm{CO_3^{2-}} \tag{3.10}$$

where Me represents the metal ion such as Ca, Mg and Ba (Plummer et al., 1978; Chou et al., 1989; Wollast, 1990; Pokrovsky et al., 2005).

The dissolution of most clay (aluminosilicate) minerals also release base cation (Fe(II), Ca, Mg),and alkali elements such as Na and K, which leads to H+ consumption, and contribute to the dissolved Al and Si found in the tailings pore water (Blowes & Ptacek, 1994). However, Al and Si dissolution rates are significantly smaller than that of carbonate minerals. In contrast with carbonate minerals that are categorized in dissolving mineral group with a relative reactivity of one, clay minerals such as kaolinite are grouped in the slow weathering category with a relative reactivity value of 0.02 (Jambor and Blowes, 1998). Reactions 3.11 and 3.12 describe kaolinite dissolution under acidic and basic conditions, respectively, and reaction 3.13 describes illite dissolution under an acidic condition (Huertas et al., 1998; Köhler et al., 2003; Cama and Ganor, 2015):

$$\mathrm{Al_2Si_2O_5(OH)_4 + 6\,H^+ \leftrightarrow 2\,Al^{3+} + 2\,H_4SiO_4 + H_2O} \qquad (3.11)$$

$$\mathrm{Al_2Si_2O_5(OH)_4 + 5\,H_2O + 2\,OH^- \leftrightarrow 2\,Al(OH)_4^- + 2\,H_4SiO_4} \qquad (3.12)$$

$$\mathrm{(Si_{3.55}Al_{0.45})(Al_{1.27}Fe^{(III)}_{0.36}Mg_{0.44})O_{10}(OH)_2(Ca_{0.01}Na_{0.13}K_{0.53}) + 7.80\,H^+ \leftrightarrow}$$
$$\mathrm{3.55\,SiO_2 + 1.72\,Al^{3+} + 0.36\,Fe^{3+} + 0.44\,Mg^{2+} + 0.01\,Ca^{2+} + 0.13\,Na^+ +}$$
$$\mathrm{0.53\,K^+ + 4.90\,H_2O} \qquad (3.13)$$

Quartz is a typical gangue mineral in coal which is categorized in the inert group by a relative reactivity value of 0.004 (Jambor and Blowes, 1998). Huggins et al. (2012) summarized the dissolution rate order based on column leach tests conducted on various coal waste streams. The dissolution rate order for the associated minerals was: calcite > pyrite >> clay minerals.

As discussed, coal waste streams are comprised of a variety of minerals which have differential dissolution rates. The dissolution of a few minerals results in undesirable environmental conditions which is reflected by high or low pH conditions, elevated total dissolved solids (TDS) content, and high electrical conductivity in the supernatant water. The minerals also differ in their physical properties including crystalline size and density. As a result, mineral types are naturally segregated in a coal preparation plant into the various reject streams and specially designed circuits can be employed to concentrate and isolate specific minerals in an effort to remediate environmental concerns regarding coal waste disposal. However, fractionating each waste stream by particle size and density results in a large number of samples that would require significant time and resources to evaluate leaching characteristics using standard column leaching experiments. Electrical conductivity measurements can be used as a means of providing timely assessments of the various fractions in a coal waste material. In this screening process, fractions with high electrical conductivity may be considered as an environmental concern while materials providing a low conductivity can be studied in more detail using long-term column leaching tests.

The application of a conductivity-screening level (CSL) test was utilized to characterize coal waste streams and identify fractions that contribute to the elevation of TDS and thus the EC values. The processing waste material was separated into a number of particle size and density fractions and subjected to the CSL tests to identify the components that would cause environmental harm if handled and stored in a conventional manner. The test program also investigated the potential of liberating the environmentally harmful minerals to minimize the material requiring isolation. The positive effects of liberating the minerals that provide natural buffering capability was also studied and the results reported in this chapter.

3.2 Experimental

3.2.1 Sample Collection and Characterization

A comprehensive set of representative samples were collected by taking incremental samples every 20 minutes over a four hour operating period during a typical operating shift at a coal processing plant. The plant was located in northern Appalachia and utilized various circuits to treat coal that was extracted from the Pittsburgh No. 8 coal seam, which was classified as high volatile bituminous coal containing a relatively large amount of sulfur in pyritic form.

Dense medium vessels and cyclones were utilized for treating the coarse (+10 mm) and intermediate (10 x 1 mm) particle size fractions, respectively. Spiral concentrators were used for cleaning the fine size fraction (1 x 0.15 mm). The ultrafine material which consisted of particles smaller than 0.15 mm was upgraded using a froth flotation circuit.

As shown in Figure 3.1, the representative samples were collected from the following process streams: 1) plant feed, 2) plant clean coal, 3) dense medium vessel refuse (DMVR), 4) dense medium cyclone refuse (DMCR), 5) high frequency overflow (HFO), 6) total coarse refuse (TCR), which includes DMVR, DMCR, and HFO, 7) thickener underflow(TU), and 8) the discharge stream for the fine refuse sump (FRS), which includes TU and high frequency underflow.

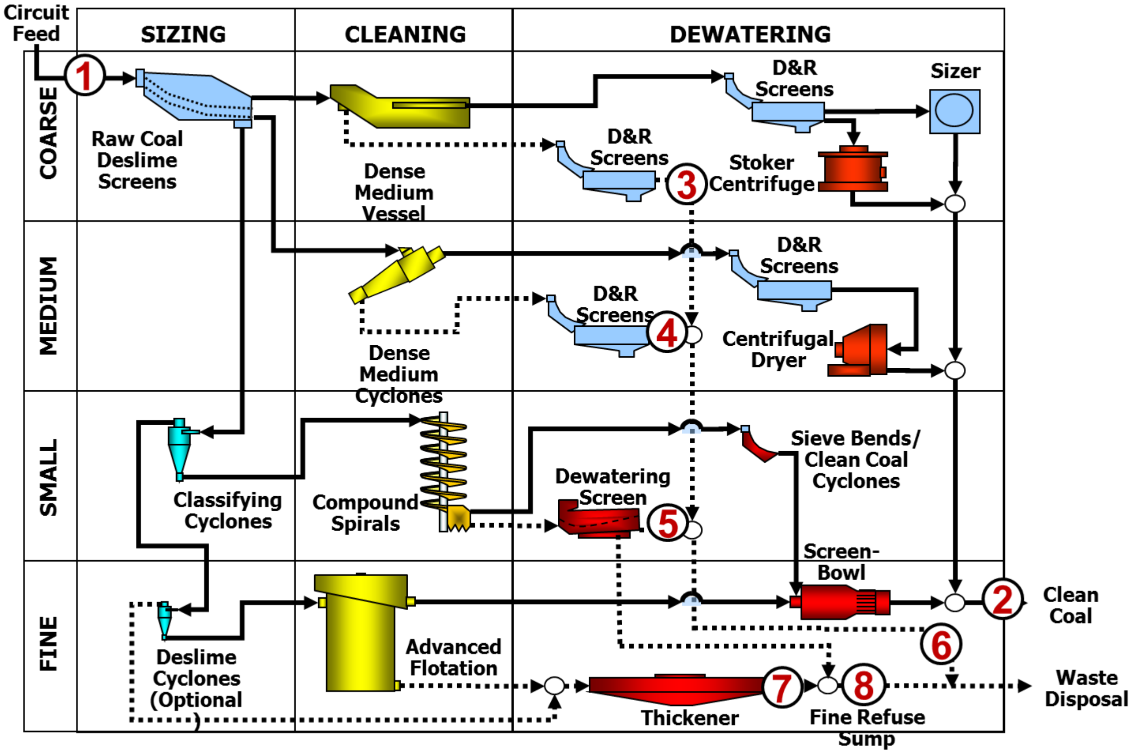


Figure 3.1. Sampling locations in the coal processing plant: 1) Feed, 2) Clean coal, 3) Dense medium vessel refuse, 4) Dense medium cyclone refuse, 5) High frequency overflow, 6) Total coarse refuse, 7) Thickener underflow, and 8) Fine refuse sump.

Upon arrival at the laboratory, the DMVR, DMCR and HFO were spread out and air-dried over a period of about 3 days. For the DMVR and DMCR samples, the coning and quartering method was employed to split the sample into representative sample lots comprising of the original particle sizes. The coning and quartering involved heaping the bulk sample into a pile and dividing into four quarters, rejecting two opposite quarters, mixing the two remaining quarters and then repeating the process until a suitable volume of material remained for splitting. Afterwards, the representative samples were stored in large vacuumed plastic bags for analysis and CSL test.

To evaluate the impacts of liberation, the top particle size of the DMVR and DMCR samples was further reduced using a laboratory jaw crusher and, in some cases, a hammer mill to pre-selected top sizes ranging from 38.1 to 1mm. After mixing the ensure homogeneity, representative samples from each top size lots were obtained for a CSL test and size-density fractionation. A laboratory Jones riffle splitter was employed for this process which yielded 1 kg sample lots to be used for analysis and the experimental program. After riffling, the final samples were stored in vacuumed sealed bags to prevent atmospheric oxidation. The clean coal sample was processed in the same manner except for the air drying step. Also, given that the top particle size of the high frequency screen material was 1mm, no crushing was required prior to splitting into representative samples.

The fine refuse and thickener underflow slurry samples were well mixed for 15 min using an agitator and split into several representative slurry samples using an Outotec Rotary Slurry Sampler Model WS-220. One of the samples was used to measure the initial slurry pH and conductivity as well as the solids content and trace element concentrations in the supernatant liquid. A particle size analysis was also conducted on a representative sample using a wet sieve screening procedure. The remaining sample was filtered using a pressure filter and dried in a low temperature oven for 24 hours. The dried samples were then crushed using a hammer mill equipped with an internal screen having 1 mm apertures. The crushed samples were then split into representative lots and stored until use in the experimental program.

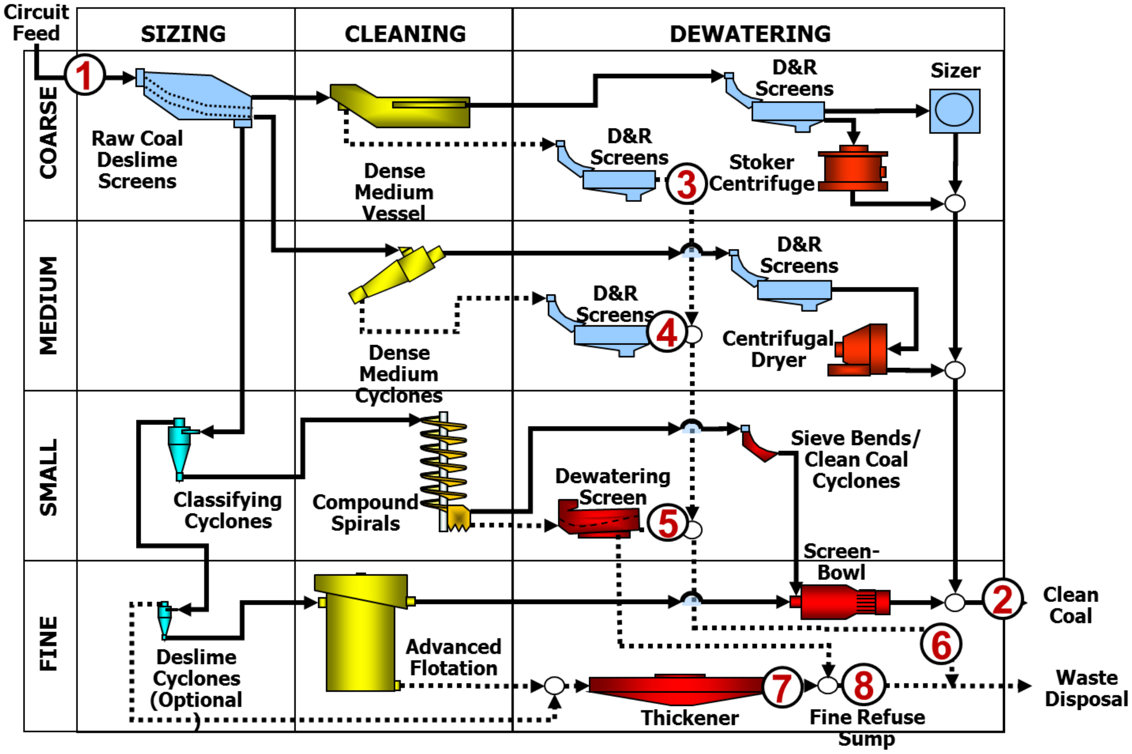


Figure 3.2. Sampling locations in the coal processing plant: 1) Feed, 2) Clean coal, 3) Dense medium vessel refuse, 4) Dense medium cyclone refuse, 5) High frequency overflow, 6) Total coarse refuse, 7) Thickener underflow, and 8) Fine refuse sump.

After the required preparation, the samples were analyzed for their particle size distribution, ash content, sulfur forms, major elements using XRF, and elemental analysis by Inductivity Coupled Plasma – Optical Emission Spectroscopy (ICP-OES). The particle size distributions provided in Figure 3.2 show that the dense medium vessel and cyclone reject materials were relatively coarse as expected with top sizes of 100 and 20 mm, respectively, and a bottom size of around 1 mm. The high frequency screen (HFS) overflow is the reject material derived from a cleaning circuit treating nominally 1 x 0.15 mm which is reflected by the size distribution. The smallest particle size distributions with more than 80% finer than 0.15 mm were associated with the fine reject and thickener underflow samples with the latter being the finest.

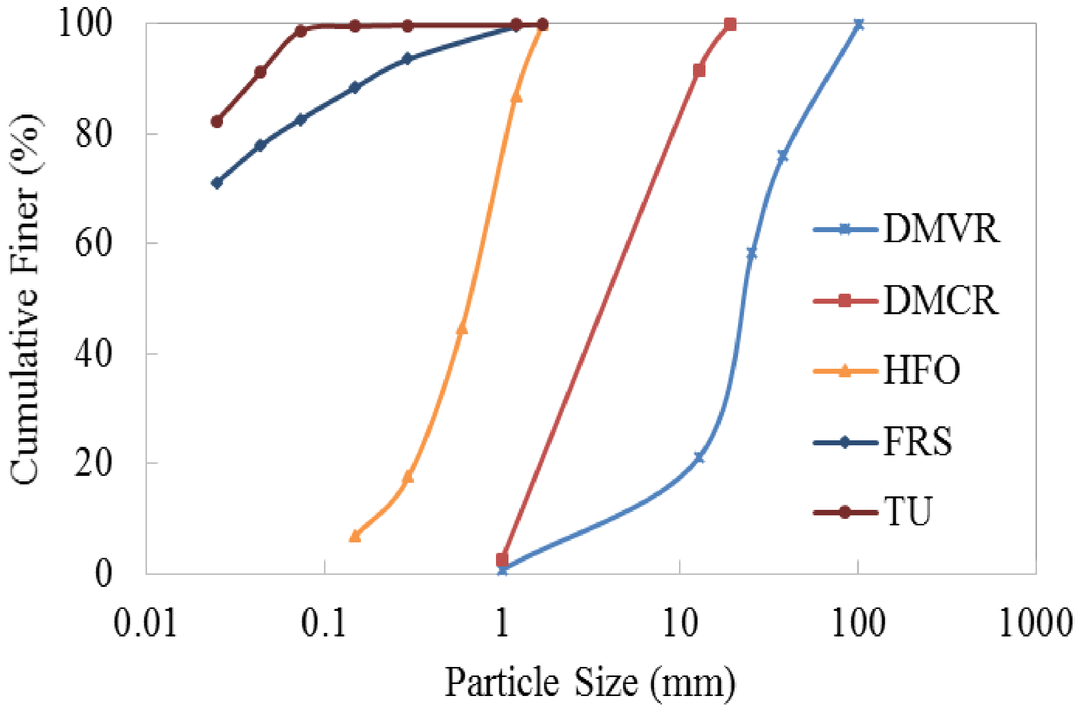


Figure 3.3. Particle size distributions of the dense medium vessel refuse (DMVR), dense medium cyclone refuse (DMCR), high frequency overflow (HFO), fine refuse sump (FRS) and thickener underflow (TU) samples.

The total ash contents and sulfur forms for each sample are provided in Table 3.1. The Pittsburgh No. 8 coal feeding the coal preparation plant was found to contain 22.59% ash bearing material and 2.84% total sulfur of which the pyritic-to-organic ratio was approximately 1:1. As expected, the material in the waste streams contained the highest quantities of ash and pyritic sulfur. The materials in the coarse waste streams and high frequency overflow were concentrated in ash-forming minerals with contents exceeding 75% as well as pyrite as indicated by high relatively high pyritic-to-organic sulfur ratios. The dense medium cyclone refuse and high frequency screen overflow streams were particularly high in pyritic sulfur due to liberation and classification of the fine pyrite into the underflow of the cyclones used to achieve sizing and density-based separations. The lower pyrite content in the coarse dense medium vessel reject was due to the dilution of coarse rock from out-of-seam sources during the extraction of the coal. The lower ash and sulfur contents in the fine reject reflected the inefficiencies of the cleaning processes used to process the fine particle size fractions which resulted in significant coal loss and dilution of the mineral matter.

Table 3.1. Ash and sulfur contents including sulfur forms in the materials collected from the various process streams of an operating coal preparation plant.

Sample No.	Sample Description	Ash (%)	Sulfur Forms (%)			
			Total	Sulfate	Pyritic	Organic
1	Feed	22.59	2.84	0.04	1.38	1.42
2	Clean Coal	8.9	3.09	0.03	1.22	1.84
3	DMVR	86.48	2.19	0.15	1.68	0.36
4	DMCR	79.86	4.54	0.32	3.53	0.69
5	HFO	76.04	9.88	0.08	7.79	2.01
6	TCR	81.55	5.29	0.44	4.39	0.46
7	TU	40.64	1.69	0.22	0.42	1.05
8	FRS	47.58	3.09	0.26	2.2	0.63

The major element contents of the ash forming components in each process stream are listed in Table 3.2. As expected, the large major components of the material in each stream were silica oxide and aluminum oxide likely in the form of sandstone and clay minerals. Iron content was also a significant component which was likely due to the high pyrite content. The presence of calcium oxide in significant quantities, which was an indicator of the presence of calcite, was a significant finding given its potential for providing neutralization potential (Eq. 3.7). The apparent concentration of calcium oxide content into the high frequency screen overflow has importance given that the material is nearly always mixed with the high pyritic sulfur materials in the dense medium vessel and cyclone reject streams. The fine refuse reject material has the highest percentage of calcium oxide. Due to changes in environmental regulations concerning fine slurry impoundments, a recent coal industry trend is to dewater the fine reject using high pressure filter presses and combine the filter cake with the coarse reject prior to permanent placement into storage facilities. As a result, the relatively high calcium oxide concentration in the fine reject could provide pH buffering action to counter the acid producing components of the coarse reject material.

Table 3.2. Major element analyses of the ash-forming material generated from the combustion of the material in each process stream at 500˚C.

Element Oxide	% Weight of Ash							
	Feed	Clean Coal	DMVR	DMCR	HFO	TCR	TU	FRS
SiO_2	57.30	44.07	63.73	59.12	52.45	58.96	58.06	55.49
Al_2O_3	21.75	21.81	25.77	23.98	21.43	23.83	24.74	23.04
Fe_2O_3	10.18	21.13	4.54	7.86	15.19	9.58	3.35	9.43
CaO	2.52	3.78	0.67	1.59	3.69	1.53	2.74	3.98
MgO	0.90	0.72	0.69	0.74	0.66	0.71	0.98	0.94
Na_2O	0.91	0.64	0.54	0.50	0.41	0.47	2.16	1.16
K_2O	1.88	1.46	2.08	1.98	1.78	1.91	2.12	2.01
P_2O_5	0.21	0.37	0.16	0.17	0.19	0.19	0.17	0.20
TiO_2	1.23	1.05	1.33	1.21	1.06	1.20	1.15	1.09
BaO	0.05	0.08	0.04	0.04	0.04	0.04	0.05	0.05
SrO	0.06	0.16	0.03	0.03	0.04	0.03	0.05	0.05
SO_3	2.74	3.27	0.52	1.29	0.90	1.33	3.41	2.70

3.2.2 Conductivity Screening Level (CSL) Test:

The conductivity of water after contact with the coal waste sources was evaluated using the modified CSL test described in Chapter 2 which included the following steps:

1- Particle Size analysis of the sample by sieving to determine the top and bottom size of the sample, and to provide the information needed to calculate the geometric mean diameter.
2- Particle density measurement
3- Surface area calculation using the Equation 2.1.
4- Mixing a predetermined amount of deionized water with the representative coal reject sample to achieve a liquid volume-to-surface area ratio of 1:1.
5- Agitation of the water and solid mixture in a capped container for 15 min.
6- Conductivity measurement of the supernatant after allowing time for the solid particles to settle to the bottom of the container.
7- Filtration of the solid-liquid mixture to collect the supernatant for additional testing.

The CSL test was initially performed on representative samples of the original coal waste to identify which sources release more total dissolved solids (TDS) when contacted with water. Subsequently, representative sample lots of the coarse reject sources (DMVR and DMCR) were crushed down to different top sizes using a laboratory jaw crusher and hammer-mill and the products evaluated by the CLST. The study provided an assessment of the impact, positive or negative, of liberating the various minerals comprising the reject. Subsequently, the crushed samples were screened and density fractionated which provided a separation of the minerals into different fractions. As a result, the particle size and density fractions in the original and crushed coal reject fractions causing a positive or negative impact on the environment could be identified. The components that were determined to have a negative impact on the environment can be isolated through a particle size and density separation process and treated to remedy the environmental issues.

The specific sample preparation procedure involved dry sieving the samples to obtain size fractions having specific top and bottom sizes. Each particle size fraction was then separated into different density fractions by laboratory float-sink testing using lithium metatungstate salt solutions with different specific gravities. The specific gravity (SG) values of the solutions were 1.8, 2.68, and 2.95. These specific gravity values were selected based on the solid SG values of the mineral components that typically comprise bituminous coals in the Appalachian coal fields. The 1.8 SG value was chosen to concentrate the organic material in the float fraction, the 2.68 SG value to float quartz (SG = 2.65), kaolinite (SG = 2.6) and a portion of the illite (SG range = 2.6 – 2.9), the 2.95 SG value to recover the remaining illite and calcite (SG = 2.71) while isolating the pyrite (SG = 5.0) into the material that sinks in the 2.95 SG medium. Figure 3.2 provides a schematic description of the sample preparation process. If the results show that isolating specific fractions of the reject materials would be environmental beneficial, circuitry can be added to an existing processing plant at a relatively low cost to achieve the desired particle size and density separations.

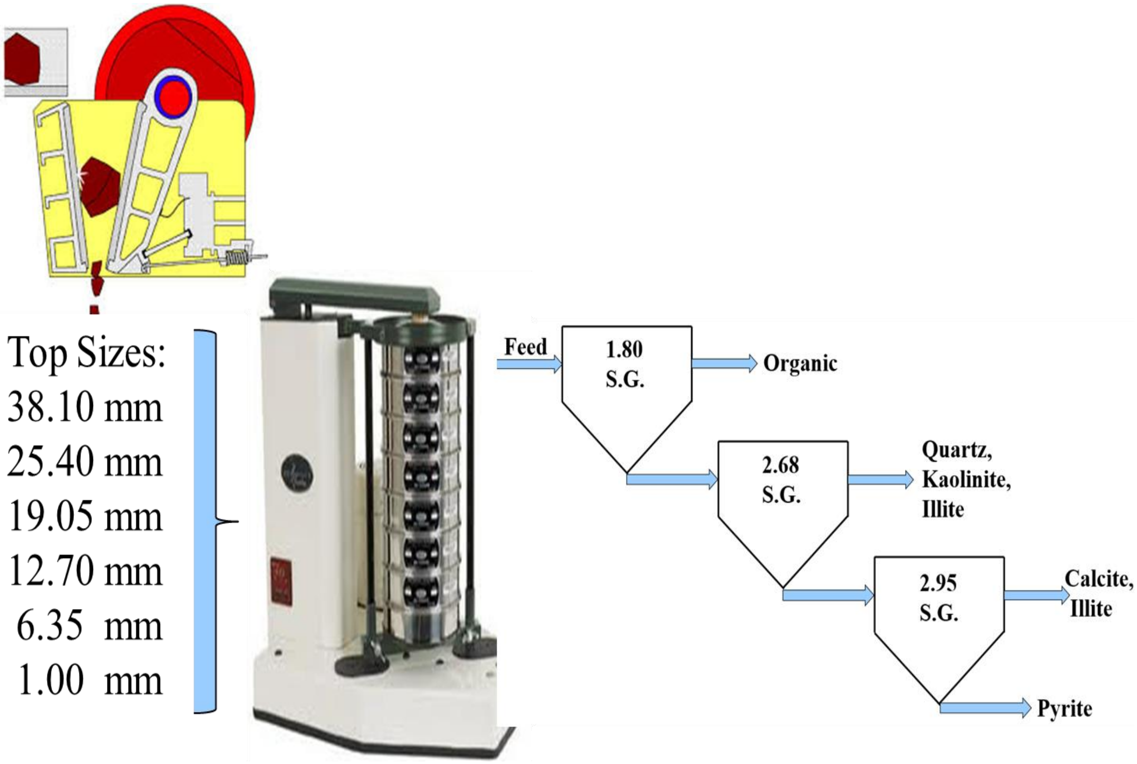


Figure 3.4. Schematic showing the sample preparation process used to assess the potential of isolating environmentally sensitive components.

3.3 Results and Discussion:

3.3.1 CSLT of refuse streams

Representative samples from the waste streams were subjected to the CSLT (Table 3.3). The high buffering capability of the HFO, FRS, and TU neutralized the pH of the supernatant liquid (D.I. water with pH of 5.7 and zero conductivity) that was in contact with the samples. As a result , acid generation reactions (Eqs. 3.1 to 3.5) were suppressed thereby preventing the release of trace elements and decreasing the TDS and conductivity (Eq. 3.7 and 3.8). On the other hand, the coarse reject generated by the dense medium vessel and cyclone was found to produce an acidic condition which resulted in an elevation of the TDS as indicated by high leachate conductivity values.

Table 3.3. CSLT results from the analysis of samples collected from the original refuse streams.

Sample	DMVR		DMCR		HFO		FRS		TU	
Measurements	EC (µS/cm)	pH	EC (µS/cm)	pH	EC (µS/cm)	pH	EC (µS/cm)	pH	EC (µS/cm)	pH
Mean	5280	2.78	1479	2.90	98.0	7.02	13.1	8.30	6.5	6.41
Standard Deviation	2376	0.22	33.2	0.01	0.2	0.64	1.1	0.40	4.9	0.05

The high frequency overflow material has an alkali and alkaline elemental content that is sufficiently high to buffer the pH and counter the effects of the high pyrite content. However, the material is typically blended into the coarse reject streams which dilutes its natural buffering capacity. The problem is magnified by the fact that the high frequency overflow material has the highest pyritic sulfur content (Table 3.1) among all reject streams which will contribute to the potential for acid generation.

A comparison of the fine refuse and thickener underflow content analysis in Tables 3.1 and 3.2 shows that the high frequency underflow also has elevated contents of calcite and coal pyrite. The pyrite contents of both the high frequency overflow and underflow are particularly high. From Figure 3.1, it is shown that the feed to the high frequency screen is derived from the tailings of the primary spiral unit. As such, a potential solution for any long term storage issues would involve the use of a mineral spiral concentrator to separate and isolate the pyrite in the high density stream of the primary spiral concentrator.

The results in Table 3.3 also suggest that coal fine refuse stream is of less environmental concern than coarse refuse. It is also implied that most of the trace elements release from impoundments is due to the passing of the water through the embankment of the impoundment, which indicates that separation and isolation of the environmentally concerned fractions of the coarse refuse streams should be performed prior to dispose in refuse piles or construction of the embankment.

3.3.2 Crushing Effect

Some of the minerals that provide natural neutralization capacity may not be liberated in the coarse reject material. As such, experiments were conducted to investigate the potential of creating natural neutralization potential by crushing the material to a smaller particle top size. Mineral liberation could result in a higher dissolution of alkali and alkaline earth elements through interactions with the solution (eq. 3.8 to 3.10), formation of insoluble sulfate minerals (eq. 3.6 and 3.7) and pH stability at values close to neutral thereby leading to a reduction in trace element mobility and conductivity. Crushing the dense medium vessel and cyclone refuse materials to a 1mm top size resulted in an increase in the supernatant liquid pH (Table 3.4 and 3.5) and a significant reduction of the conductivity level (Figure 3.5). However, the positive effects of creating natural neutralization potential through particle size reduction may be a short term effect due to the limited amounts of minerals with dissolutions rates and alkali and alkaline earth elements contents that are needed to counter the effect of pyrite oxidation.

Table 3.4. Effect of crushing on pH of supernatant liquids in contact with various top size samples of dense medium vessel refuse (DMVR) sample.

DMVR Samples	pH	
	mean	standard deviation
Origin	3.36	1.01
38.1(mm) TS	4.08	0.95
25.4(mm) TS	3.84	0.54
19.05(mm) TS	3.94	0.28
12.7(mm) TS	3.71	0.05
6.35(mm) TS	4.02	0.49
1mm TS	5.21	0.01

Table 3.5. Effect of crushing on pH of supernatant liquids in contact with various top size samples of dense medium cyclone refuse (DMCR) sample.

DMCR Samples	pH	
	mean	standard deviation
Origin	2.90	0.01
12.7(mm) TS	2.97	0.01
6.35(mm) TS	3.60	0.42
1mm TS	4.37	0.04

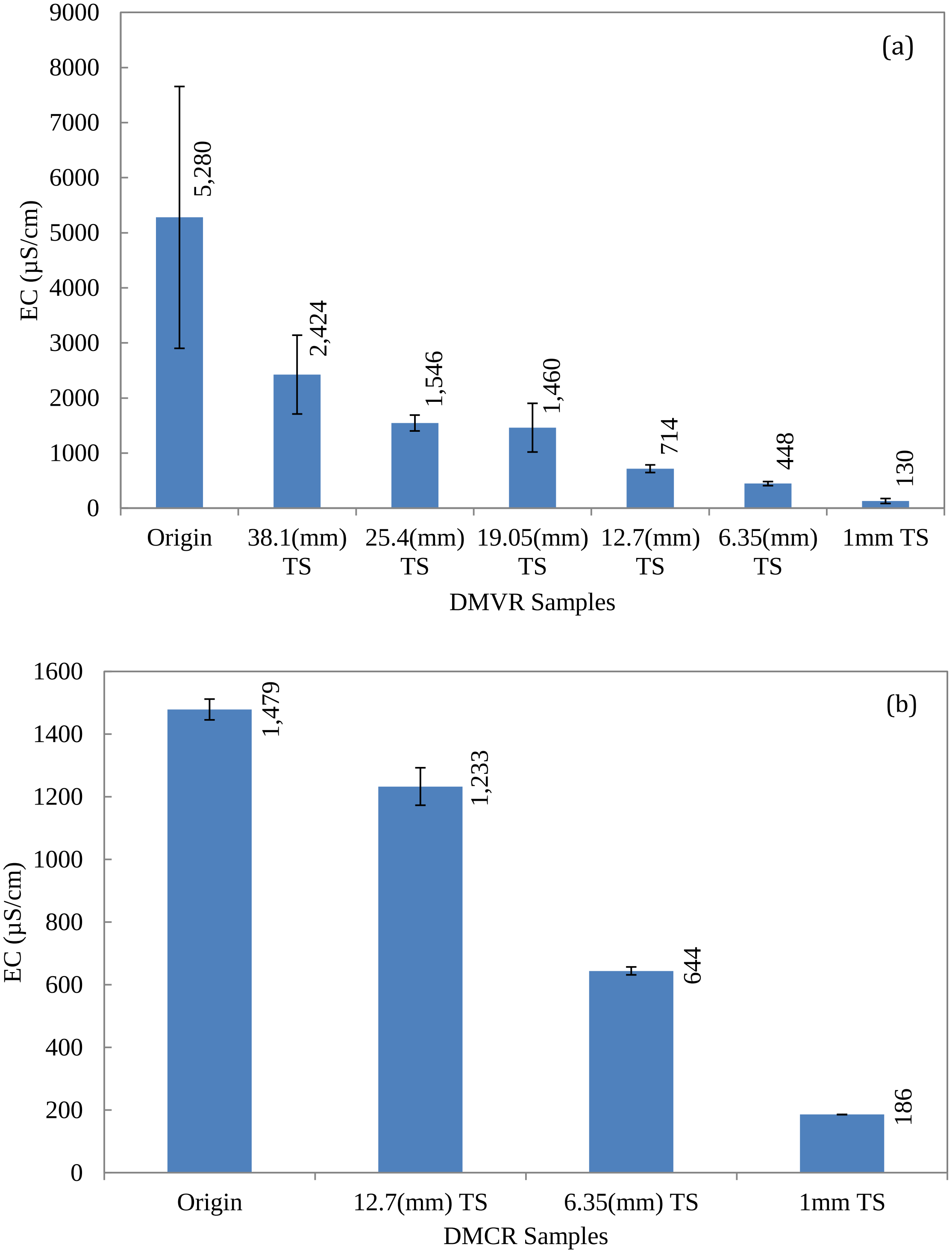


Figure 3.5. Effect of crushing on EC of supernatant liquids in contact with various top size (TS) samples of (a) dense medium vessel refuse (DMVR) and (b) dense medium cyclone refuse (DMCR).

3.3.3 CSL test on size-density fractions

Conducting CSL tests were performed on particle size-by-size density fractionated samples having different top sizes to experimentally identify the high conductivity generating fractions that need to be separated and isolated as well as to quantify the impacts of liberating the minerals by particle size reduction.

Most of the particle size and density fractions in the original sample provided elevated EC values in the supernatant liquid after mixing with the solid material as shown in Figures 3.6 (a). As a baseline, the EC and pH values of the ultrapure deionized water that was mixed with the solids in this study were zero μS/cm and 5.5, respectively. The relatively high EC values could be due to both dissolution of certain minerals and oxidation of the pyrite. For particles size fractions smaller than 25.4 mm, the pH values of the supernatant liquid samples that were mixed with the 2.68 x 2.95 SG and 2.95 SG sink fractions were below 4.0 which was proof of pyrite oxidation. On the other hand, particle sizes larger than 25.4 mm along with those in the 1.8 SG fraction of the 25.4 x 12.7 mm size class provided elevated pH conditions with values reaching 8.38. The EC value of the liquid at pH 8.38 was around 2800 μS/cm which may be a result of the release of alkali and alkaline earth elements from the dissolution of various mineral types.

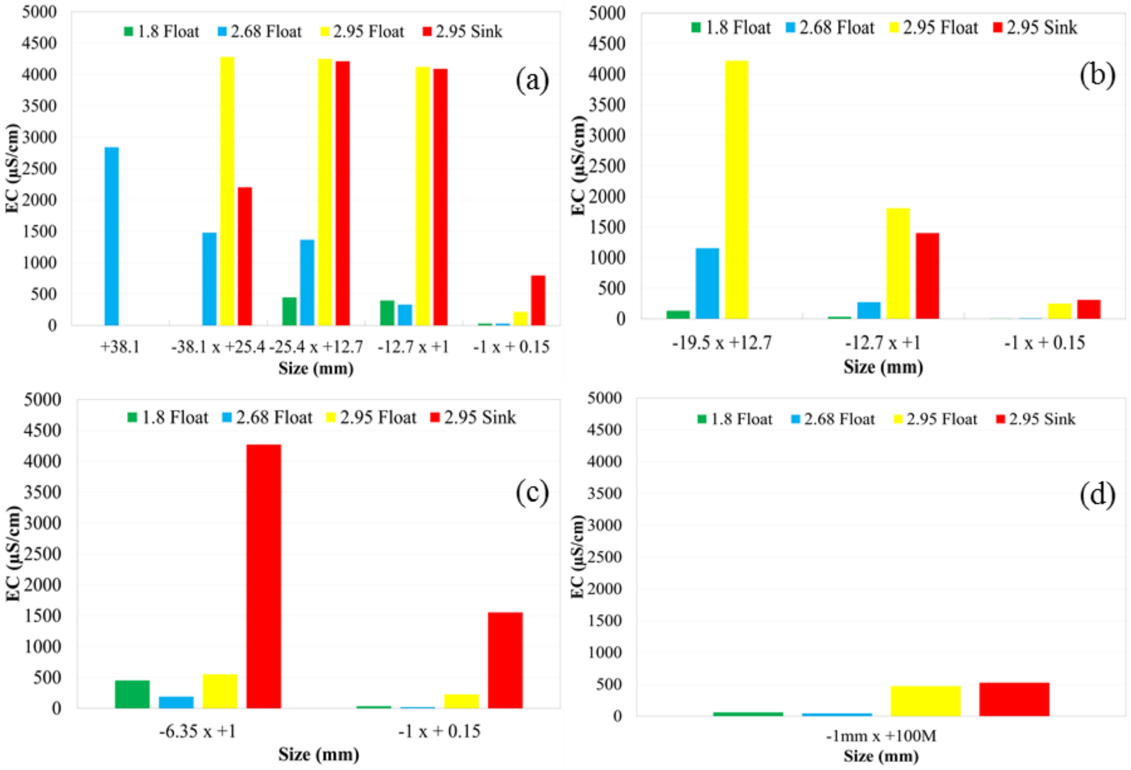


Figure 3.6. EC of supernatant liquids in contact with dense medium vessel refuse (DMVR) samples in CSL tests: (a) origin, (b) 19.2 mm TS, (c) 6.35 mm TS, and (d) 1 mm TS (TS: top size). The absence of bars for a given specific gravity fraction indicates that no material was recovered.

The original sample was crushed to a lower particle top size in an effort to quantify the impact of liberating the various minerals comprised in each density fraction. Size reduction to a top size of 19.5 mm resulted in a significant reduction in the EC values in almost all particle size and density fractions as shown by a comparison of Figures 3.6 (a) and (b). Figure 3.6(b) also shows that the EC values of the supernatant liquid dropped in each subsequently smaller particle size fractions and lower specific gravity fractions. The trend with specific gravity corresponds well with pH as shown in Table 3.7. The supernatant liquid pH values from mixing with the 1.8 SG material were in the range of 6 to 7 while the values for the 2.68 x 2.95 SG and 2.95 sink were below 4.

Table 3.6. Weight distribution of size-density fractions of DMVR sample along with associated leachate pH in CSL test.

Particle Size Fractions (mm)	Weight (%)				pH			
	1.8 Float	2.68 Float	2.95 Float	2.95 Sink	1.8 Float	2.68 Float	2.95 Float	2.95 Sink
+38.1	0.00	23.94	0.00	0.00		5.81		
38.1 x 25.4	0.00	15.55	0.32	1.91		6.48	7.64	7.40
25.4 x 12.7	0.89	35.38	0.45	0.56	8.38	5.69	5.54	4.27
12.7 x 1	0.20	19.47	0.18	0.46	5.49	5.46	3.31	3.20
1 x 0.15	0.03	0.50	0.02	0.02	5.96	6.72	5.36	4.39
Crushed to 19.5 mm top size								
19.5 x 12.7	1.08	42.79	0.49	0.00	7.00	5.57	3.11	
12.7 x 1	1.19	46.96	0.77	2.04	6.29	5.23	3.37	3.55
1 x 0.15	0.14	2.82	0.04	0.08	6.90	5.14	3.99	3.94
Crushed to 6.35 mm top size								
6.35 x 1	1.42	52.95	0.23	1.98	4.02	5.48	5.37	2.58
1 x 0.15	2.04	31.31	0.17	1.52	5.10	5.15	4.52	3.17
Crushed to 12.7 mm top size								
1 x 0.15	4.96	61.05	0.75	2.29	5.25	5.93	4.50	2.89

Further reductions in the top particle size to 6.35 mm and 1 mm continued the decrease in the EC values as shown in Figures 3.6 (c) and (d). Overall, the maximum EC values in any fraction of a sample decreased from slightly higher than 4000 μS/cm in the original sample to values below 500 μS/cm in the material having a top particle size of 1 mm.

The relatively low EC values for the finest size-density fractions (1 × 0.15 mm) were a result of the liberation of different minerals and their effective separation into the different densities. Thus, the EC value obtained for each fraction was reflective of the trace elements associated with the minerals comprised within each fraction. In other words, the lower EC values of the 2.95 sink in the finest particle size fraction relative to the larger size fraction is due to the effective liberation and separation of other minerals out of this fraction, As such, the EC value of the supernatant liquid was impacted by the release of calcophilic trace elements associated with pyrite. The EC value of this fraction increased in the larger particle size fractions since the other types of minerals such as clay minerals may remain in that fraction due to lack of liberation and effective separation. The release of lithophilic trace elements associated with the clay minerals (Eq. 3.11 to 3.13) also elevates the TDS and EC values of those fractions.

The same explanation would apply for lower EC levels for fractions in the samples with top sizes smaller than 6.35 (Figure 3.6 (c) and (d)). The low EC levels in the 1.8 float and 2.95 float fractions is due to the very low relative dissolution rate of the mineral content (clay, quartz and organic materials) in such fractions. Medium level of EC in 2.95 float is expected to be due to high dissolution rate of calcite while the high EC level of 2.95 sink was due to the oxidation of pyrite and release of elements associated with pyrite into the supernatant liquid. The effective separation of minerals in such samples to different densities can be also seen by the larger difference in the pH values (3.7).

Materials having a particle size smaller than 0.15 mm that were excluded from the float and sink analysis showed low level of EC (Table 3.6). This could be due to the high exposure of the buffering capability of the sample to the solution due to the ultrafine size and high surface area for dissolution which suppress the release of elements.

Table 3.7. Characteristics of -0.15 mm fraction of DMVR samples.

Characteristics	-0.15 mm fraction of DMVR samples						
	Origin	38.1 mm TS	25.4 mm TS	19.5 mm TS	12.7 mm TS	6.35 mm TS	1 mm TS
Weight (%)	0.13	1.6	0.65	1.61	2.38	8.37	30.95
EC (µS/cm)	39.6	23.9	10	8	9	7	25
pH	4.58	4.04	5.02	5.11	4.76	4.47	4.2

The weight percentage of high and medium-level generating EC is less than 5% after liberation, i.e. 3.9% and 3.04 % for 6.35 mm and 1 mm top size samples, respectively (Table 3.7).

The impact of particle size reduction on reducing the EC values associated with the Dense Medium Cyclone Refuse (DMCR) followed the trends described by the dense medium vessel reject results as shown by Figures 3.7 (a) through (b). The 2.95 sink fractions were the only fractions generating high EC values after the DMCR samples were crushed to top sizes of 6.35 and 1 mm (Figure 3.7 (c) and (d)). The weigh percentage of the 2.95 density fractions were also close to 5%, i.e. 4.40% and 5.38% for the 1 and 6.35 mm top size samples (Table 3.8).

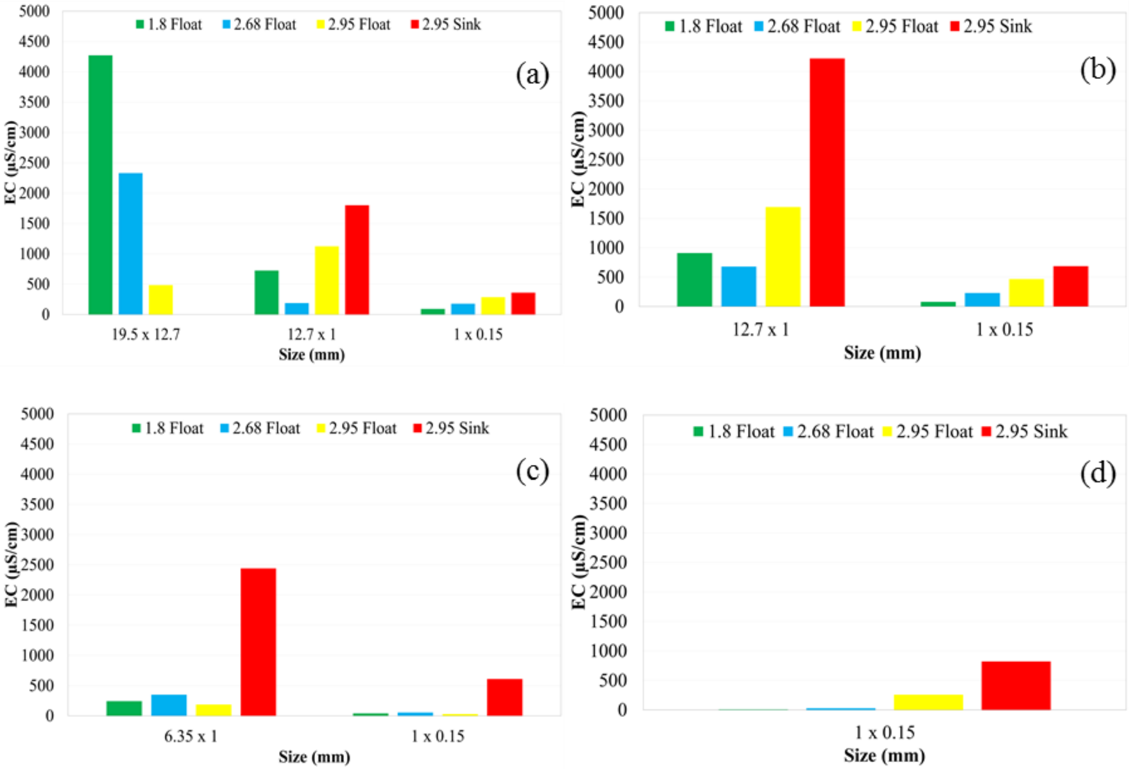


Figure 3.7. EC of supernatant liquids in contact with DMCR samples in CSLT (a) origin, (b) 12.7 mm TS, (c) 6.35 mm TS, and (d) 1 mm TS. . The absence of bars for a given specific gravity fraction indicates that no material was recovered.

Table 3.8. Weight distribution of size-density fractions of DMCR sample along with associated leachate pH in CSL test.

Particle Size Fractions (mm)	Weight (%)				pH			
	1.8 Float	2.68 Float	2.95 Float	2.95 Sink	1.8 Float	2.68 Float	2.95 Float	2.95 Sink
19.5 x 12.7	0.66	7.93	0.03	0.00	1.67	2.96	NE*	………………..
12.7 x 1	9.63	74.61	1.12	3.46	2.87	4.19	3.30	2.27
1 x 0.15	0.31	1.90	0.03	0.13	4.42	4.26	3.14	2.86
Crushed to 12.7 mm top size								
12.7 x 1	10.22	82.63	1.27	2.93	2.57	3.01	2.33	1.34
1 x 0.15	0.30	2.29	0.05	0.13	4.16	3.99	3.64	3.03
Crushed to 6.35 mm top size								
6.35 x 1	4.65	51.03	0.45	3.03	3.27	3.45	3.44	2.37
1 x 0.15	4.92	26.72	0.44	2.35	6.05	6.20	4.22	2.85
Crushed to 1 mm top size								
1 x 0.15	10.78	58.68	1.21	4.40	7.07	6.81	3.58	2.85

*NE: not enough sample for analysis

Size fractions finer than 0.15 mm also generated low conductivity values for the DMCR samples (Table 3.9).

Table 3.9. Characteristics of -0.15 mm fraction of DMCR samples.

Characteristics	-0.15 mm fraction of DMVR samples			
	Origin	12.7 mm TS	6.35 mm TS	1 mm TS
Weight (%)	0.19	2.76	6.41	24.93
EC (µS/cm)	17	14	5	2
pH	5.54	4.75	4.93	4.92

High frequency overflow (HFO) samples contained higher amounts of liberated pyrite and calcite than other coarse refuse streams (Tables 3.1 and 3.2). As a result, the higher density fractions (2.95 float and sink) in the HFO samples generated high EC levels, especially in coarser particle size fractions (Figure 3.8) while low EC levels were measured in the supernatant after interaction with the material in the lower density fractions, which contain minerals that have low dissolution rates. The 2.95 SG float and sink fractions account for 14.46% of the total HFO waste stream (Table 3.10).

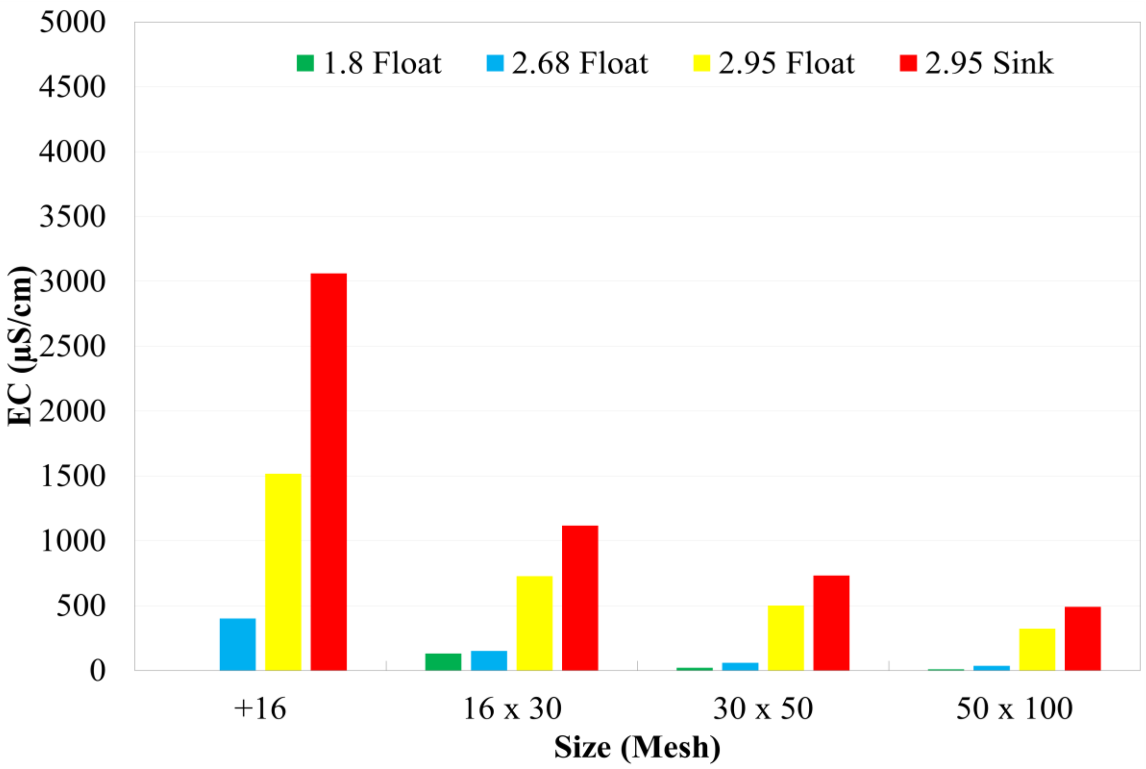


Figure 3.8. EC of supernatant liquids in contact with the size-density fractions of HFO.

Table 3.10. Weight distribution of size-density fractions of HFO sample along with associated leachate pH in CSL test.

Particle Size Fractions (mesh)	Weight (%)				pH			
	1.80 Float	2.68 Float	2.95 Float	2.95 Sink	1.8 Float	2.68 Float	2.95 Float	2.95 Sink
+16	0.00	10.50	0.67	2.03		3.57	4.05	2.27
16 x 30	1.38	34.20	0.74	5.90	3.91	4.13	3.53	2.94
30 x 50	3.09	20.49	0.25	3.27	4.58	5.10	3.80	3.04
50 x 100	2.85	6.09	0.17	1.43	5.10	5.47	3.57	3.01
-100	6.93				7.47			

3.4 Material Segregation

In current coal waste disposal practices, the dense medium vessel and cyclone reject streams along with the high frequency screen overflow which is comprised of mostly spiral concentrator reject material are combined and disposed as the total coarse refuse stream. The CSL test results indicated that the high specific gravity fractions (i.e., 2.68 x 2.95 SG float and 2.95 SG sink), the EC values in the water contacted the solid surfaces were elevated due to the release of elements associated with pyrite in these density fractions.

To quantify the amount of material that is primarily responsible for the negative effects of high EC and low pH values, consider the throughput capacity of 1600 tph for the plant where the samples were collected. The mass yield (mass percentage of the plant feed reporting to the clean coal product stream) of the plant is 78%, which is a typical yield for coal processing plants. As such, 1244 tph of the plant feed reports to the clean coal stream, 258 tph to coarse refuse and 98 tph to the fine refuse streams. In the coarse refuse streams, 40% and 54% report from the dense medium vessel and dense medium cyclone separation units, respectively, while the remaining 6% material reports to the coarse refuse streams through the high frequency overflow stream. Using the density-by-density weight distribution data for each sample in Table 3.11, the weight percentages of the density fractions of the coarse refuse stream and its sub-streams, indicate that only less than 10% of the total materials (2.95 sink and 2.95 float) in the coarse refuse stream results in significant abatement of the electrical conductivity of the leachate from the coal waste streams.

Table 3.11. Weight distribution of the density fractions of the coal processing waste streams.

Sample	Weight (%)							
	6.35 mm top size				1 mm top size			
	1.8 Float	2.68 Float	2.95 Float	2.95 Sink	1.8 Float	2.68 Float	2.95 Float	2.95 Sink
DMVR	3.78	91.96	0.43	3.83	7.19	88.41	1.08	3.32
DMCR	10.22	83.08	0.95	5.75	14.36	78.16	1.61	5.86
HFO	7.87	76.6	1.96	13.57	7.87	76.6	1.96	13.57
CR	7.53	86.19	0.81	5.47	11.12	82.12	1.42	5.33

3.5 Conclusions

Dissolution and/or oxidation of minerals in coal waste streams may result in elevation of the total dissolved solids of the discharged water. If not recycled, the discharged water should be treated through physical or chemical processes to minimize the dissolved solids and heavy metals content of the water prior to discharge to the environment. Electrical conductivity can be used as an indirect measurement of the total dissolved solids. Additional, current regulations limit the EC level in certain mining regions where the EC value of the supernatant liquid has been shown to impact local aquatic life.

In this study, a conductivity screening-level test was used to compare EC values generated from the handling and storage of various coal processing waste streams. Additionally, testing was conducted to identify EC values as a function of material properties (i.e. size and density). The results showed that the EC of coarse refuse streams are much higher than fine refuse streams. Spiral refuse may require additional treatment to separate the higher generating EC fractions prior to being transferred to the high frequency screen and being combined to coarse and fine refuse streams. Results of CSL test indicated that pyrite oxidation and mineral dissolution associated with less than 10% of the coal preparation coarse refuse stream were the primary sources of high conductivity levels.. The remaining materials were not found to generate high EC levels in water. This finding is due to the fact the minerals comprised in these fractions are resistant to leaching and thus have low dissolution rates. The high generating EC fractions appear in high density fractions (SG > 2.68). The liberation and separation followed by isolation of this fraction results in significant abatement of EC, as an indicator of total dissolved solids, of the waste discharged from coal processing waste streams

4. LEACHING CHARACTERISTIC STUDY OF COAL PROCESSING WASTE STREAMS

Summary: A study of the mobility of major and potentially hazardous trace elements from coal processing waste materials was conducted using two types of leaching tests. The static leaching test simulates stable waste storage under water, whereas the dynamic test models the storage of waste under more variable conditions including intermittent exposure to air and variations in humidity. Coarse and fine refuse materials were obtained from three commercial coal preparation plants that were being used to upgrade US bituminous run-of-mine coal containing low to high amounts of pyritic sulfur. X-ray diffraction analysis revealed a large variation in mineralogy between the coarse and fine refuse streams due to the mineral fractionation that occurs in the processing units and plant. Coarse refuse contained higher pyrite content while the fine refuse samples had a high clay content and a minor amount of calcite. This variation in mineralogy resulted in large difference in the leaching characteristics of the waste streams. The most acidic pH and highest release of trace elements were observed in the leachate of high and medium pyritic coal samples, while the fine refuse samples released lower amounts of trace elements in their circumneutral leachate. The least amount of trace elements was observed in the leachate of low pyritic refuse streams. The data therefore suggest that the pyrite content of the coarse refuse streams is responsible for the acid rock drainage and release of trace elements in coal waste disposal. As a result, separation and isolation of the pyrite content of the coarse refuse streams provides significant environmental improvement in coal waste disposal.

4.1 Introduction

Upgrading run-of-mine coal is achieved by rejecting mineral matter in coal to increase the heating value and meet market qualifications. After processing, 50-70% of the run-of-mine material is rejected and placed into surface storage areas. Impoundment are used to store fine coal waste containing particles smaller 0.15 mm in slurry form. The dam is typically constructed using coarse refuse and sand from previous mining activities.

Most of the trace elements of environmental concern such as arsenic, selenium, and chromium are associated with mineral matter (Table 4.1) and therefore tend to be concentrated in the coal waste streams (Querol et al., 1995; Vejahati et al.,; Zhang et al., 2015). Two major coal minerals that contain most of the trace elements in eastern U.S. bituminous coals are illite and pyrite. Illite, a clay mineral, typically encompasses most of the lithophilic trace elements such as vanadium and chromium, while the behavior of chalcophilic elements such as arsenic, selenium, mercury and lead is typically controlled by pyrite, a sulfide mineral. A number of other elements including nickel, manganese and zinc may have a mixed association with both of the minerals (Huggins et al., 2009). A possible mobilization of these trace elements from coal waste impoundments, therefore, may be of environmental concern (Rezaee et al., 2013; Ghosh et al, 2015).

The oxidative weathering of pyrite and dissolution of carbonate and clay minerals have the potential to degrade the water quality by mobilization of metals exceeding the water quality, increasing total dissolved solids (TDS) content of water and its specific conductivity level (EC).

Table 4.1. Trace elements association in coal (after Vejahati et al., 2010).

Affinity	Mineral Group	Mineral Type	Elements
Inorganic	Clay minerals and feldspars	Kaolinite, Illite Montmorillonite	Al, Ba, Bi, Cr, Cs, Cu, Ga, K, Li, Mg, Na, Ni, P, Pb, Rb, Sn, Sr, Ta, Th, Ti, U, V, Y, and rare earth elements
	Iron sulfides	Pyrite, Sphalerite	As, Cd, Co, Cu, Fe, Hg, Mo, Ni, Pb, S, Sb, Se, Ti, W and Zn
	Carbonates	Calcite, Dolomite, Ankerite, Siderite	Ca, Co, Mn
	Sulphates	-	Ba, Ca, Fe, and S
	Heavy minerals	Tourmaline	B
Organic	N, S, Be, B, Ge, V, W, Zr, rare earth elements		

Developing new strategies to minimize the TDS and EC of supernatant liquids in contact with coal processing waste streams requires understanding of their associated leaching characteristics. Static and kinetic leaching tests have been developed to evaluate or predict the leaching characteristics of a given material (Sobek et al., 1978, O'Shay etal., 1990; Kleinmann, 2000; Chotpantarat, 2011; Parbhakar and Lottermoser, 2015). Static tests include acid base accounting (ABA) and neutralization potential (NP) while the kinetic tests utilize humidity cells, leaching columns, soxhlet reactors, shake flasks, pilot and large field leaching tanks (ASTM D5744, Danielle, 2013; Sobek et al., 1982; Renton et al., 1988; Ziemkiewicz, 2013; Renton et al., 1984).

In this chapter, the leaching characteristics of coal waste streams from U.S. processing plants treating high, medium, and low pyritic bituminous coals were examined. Two long term dynamic and static leaching testswere performed for the study. The dynamic leaching test was a variation of the ASTM standard Test Method D-5744 (ASTM, 1996) and included a weekly cycle exposure to moist and dry air followed by leaching with deionized water. This test was designed to simulate waste storage scenarios involving exposure of the material to the atmosphere, either in variable wet/dry storage condition, or unusual circumstances like breaching of an impoundment containment wall. The static leaching test, in which the material is stored under water, was designed to simulate the quiescent conditions such as those in stable impoundments.

4.2 Experimental

4.2.1 Sample Collection and Characterization

Modern coal processing plants typically consist of four processing circuits for treating the coarse (> 10 mm), intermediate (-10 x 1 mm), fine (-1 x 0.15 mm), and ultrafine (< 0.15 mm) material. Dense medium vessel, dense medium cyclone, spiral concentrators and flotation are utilized, respectively, for the separation. Various scenarios involving the type and number of operation units may be considered for processing. The selection of the operation units depends on properties of the coal and required specifications of the final product (Gluskoter, 2009; D. Osborne, 2013). Clean product streams from all the four fractions are combined as the final product. The spiral refuse stream is deslimed using a high frequency screen in which the overflow stream is combined with the coarse reject material while the underflow reports to the plant fine reject stream in the thickener underflow. The thickener underflow stream is either pumped to an impoundment or dewatered using high pressure filters and subsequently co-disposed with the coarse reject.

A set of representative samples of the coarse and fine refuse streams were collected at 20 minute time intervals over a 4 hour period from three coal processing plants treating:

1. Coalburg coal seam, Central Appalachia, WV (low pyritic content);
2. Pittsburgh No.8 coal seam, Northern Appalachia, PA (Medium pyritic content);
3. 5-B central Illinois-based coal seam, IN (High pyritic content).

After receiving the material, the coarse refuse samples were spread out and air-dried over a period of about three days. Sample preparation involved crushing to a particle top size of 12.7 mm (½-inch) using a jaw crusher. The top size was further reduced to 6.35 mm (¼-inch) by crushing using a Holmes hammer mill crusher, accompanied by a manual mixing stage to ensure homogeneity of the samples. The coning and quartering method was employed for achieving a representative reduction in sample volume. The method involved heaping the bulk of the sample in a pile and dividing into four quarters, rejecting two opposite quarters, mixing the two remaining quarters and then repeating the process until a suitable volume of material remained for splitting. A laboratory Jones riffle splitter was employed at this stage which finally yielded representative samples of about 1 kg for analysis and experiments. For splitting, samples were poured onto the top of a riffle which splits the samples using alternating angled slots that discharge into separate containers underneath the riffle. The final samples were stored in sealed bags to minimize atmospheric oxidation. The reject portion of the sample was then returned to the barrel and sealed airtight for future use.

The fine slurry refuse samples were well mixed for 15 min using an agitator prior to splitting into several representative lots using an Outotec Rotary Slurry Sampler Model WS-220. A representative split was used to assess the initial pH, conductivity, solids concentration, particle size analysis and the trace element concentration in the supernatant liquid. The remaining samples were then filtered using a pressure filter and dried in an oven for 24 hours. The dried caked samples were then passed through a hammer mill crusher with an internal screen size of 1mm to separate agglomerated clay particles from each other. A riffler was used to split the material into small representative lots. Each sample was stored in a sealed bag until use.

After the required preparation, a representative lot was was analyzed for ash content, sulfur forms, the presence of major elements using XRF, mineral matter content by X-ray Diffraction (XRD) utilizing Rietveld method and elemental analysis by Inductivity Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

The ash contents and sulfur forms (ASTM D-2492) for each sample collected from the processing plants are listed in Table 4.2. The results clearly show that the Coalburg and Pittsburg coal seam samples have relatively low and medium sulfur content, respectively, while 5-B Central coal seam samples have high sulfur content. All three samples are classified as high volatile bituminous coals. The ash contents of the coarse reject samples were higher than the fine refuse streams in all three plants which is reflective of the superior separation performances provided by the coarse cleaning units. The ash content of the 5-B Central coal seam appears relatively low which is partially due to the need to achieve a lower density separation to meet sulfur content requirements in the final product. However, the 19.39% pyritic sulfur also represents a significant portion of the mineral matter in the coarse reject stream that was combusted in the form of sulfur and thus not accounted for in the ash content value.

The pyritic sulfur content is a primary concern due to the acidity that it generates as a result of oxidation. The data in Table 4.2 indicate that the coarse refuse streams have a substantially higher pyritic sulfur content than fine refuse streams. This is due to unliberated pyrite content of dense medium vessel and dense medium cyclone, as well as the relatively high liberated pyrite content of high frequency overflow stream. The liberated pyrite content in the fine fractions (-1 x 0.15mm) of the plant feed is concentrated in the underflow of the classifying cyclone and reports to the spiral refuse, and concentrates in the high frequency screen overflow.

Table 4.2. Ash content and sulfur forms in the coarse and fine reject samples collected from three preparation plant.

Sample	Ash (%)	Forms of Sulfur (%)			
		Total	Sulfate	Pyritic	Organic
Coalburg Coal Seam					
Coarse Refuse	62.3	0.58	0.01	0.31	0.26
Fine Refuse	55.5	0.3	<0.01	0.26	0.04
Pittsburgh No.8 Coal Seam					
Coarse Refuse	81.55	5.29	0.44	4.39	0.46
Fine Refuse	47.58	3.09	0.26	2.2	0.63
5-B Central Coal Seam					
Coarse Refuse	54.5	26.14	1.32	19.39	5.49
Fine Refuse	41.7	9.02	0.62	6.91	1.5

The mixture of coal and various mineral types that have varying solid densities and liberation characteristics results in a broad weight distribution by particle size and density within a given feed coal. Given that the typical coal upgrading technology separates based on density over a given range of particle sizes, it is easy to understand the variability in mineralogy that exists in the different waste streams which is depicted in the XRD analysis data obtained for the 5-B Central Illinois coal (Table 4.3). The XRD data concurs with the sulfur forms in that the coarse reject contains an extremely large amount of pyrite. A positive finding is the presence of calcite in both the coarse and fine refuse streams which has a high dissolution rate. The dissolution results in elevated concentration of calcium ions in solution which provides the potential to counter the negative effects of pyrite oxidation.

Table 4.3. Semi-quantitative mineralogy of coal fractions obtained from an analysis of the 5-B Central Illinois coal using XRD.

Sample	%Mineral (as wt% of mineral matter)				
	Pyrite	Quartz	Illiite	Kaolinite	Calcite
Coarse Refuse	43	20	19	18	<5
Fine Refuse	23	18	36	23	<5

The XRD results also shows a relatively high concentration of clay minerals (illite and kaolinite) especially in the fine refuse. This finding was supported by the aluminum oxide and silica oxide contents shown in Table 4.4 as determined by XRF analyses. The higher clay concentrations in the fine refuse streams were a direct result of the ultrafine particle size and the classification of the clay particles into the overflow of the classifying cyclones which reports along with fine coal particles to either a flotation circuit or directly to the thickener. The mineralogy data are also consistent with the XRF data in regards to the high iron and sulfur contents in the high pyrite content samples. Higher calcium contents in the fine refuse streams were also due to the Ca content of the clay minerals as well as the Ca being released from the calcite mineral. The data suggests concentration of the fine calcite particles in the overflow of the classifying cyclone which ultimately reports to the fine refuse streams. This suggests higher buffering capability of the fine refuse stream to neutralize the pH of supernatant liquid in contact with fine refuse streams in the impoundment.

Table 4.4. Major element analyses (ash basis) of 500˚C ash prepared from the sample.

Sample	% Oxide (ash basis)*											
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	BaO	SrO	SO3
Coalburg Coal Seam												
Coarse Refuse	62.39	25.98	4.78	0.35	1.18	0.18	3.75	0.12	1.27	0.08	0.02	0.1
Fine Refuse	60.19	26.73	4.7	0.5	1.32	0.28	4.11	0.1	1.12	0.12	0.03	0.34
Pittsburgh No.8 Coal Seam												
Coarse Refuse	58.96	23.83	9.58	1.53	0.71	0.47	1.91	0.19	1.2	0.04	0.03	1.33
Fine Refuse	55.49	23.04	9.43	3.98	0.94	1.16	2.01	0.2	1.09	0.05	0.05	2.7
5-B Central Coal Seam												
Coarse Refuse	24.41	10.41	61.48	0.45	0.58	0.24	1.38	0.15	0.43	0.02	0.02	0.45
Fine Refuse	44.13	16.76	26.99	5.41	1.09	0.35	2.28	0.24	0.73	0.07	0.03	1.91

* As %wt. of mineral matter

4.2.2 Leaching Experiments

Two types of leaching tests were employed in this study which were the dynamic leaching test and the static leaching test. While the static test consisted of keeping the waste materials entirely under water for periods of up to twelve months, the dynamic test involved exposure of the waste materials in a weekly cycle to first dry air and then humid air for up to 20 weeks. The dynamic test is based on the procedure described in ASTM test method D-5744 (ASTM 1996).

4.2.2.1 Dynamic Leaching Experiment

The standard ASTM method D 5744 was designed specifically to meet regulatory requirements for mining wastes and ores (ASTM, 1996). In the experimental setup, the waste stream samples were placed into humidity cells made of PVC (Figure 4.2). The samples, each weighing 200 g, rested on 22-µm polypropylene felt filter media placed on the top of perforated PVC which served as an air distributor to allow air and water to flow through while retaining the samples. Flowmeters were used to deliver air to each humidity cell at a constant rate of 10 L/m/cell. The humidity cells were setup to receive an upward flow of air through a valve located at the bottom of cell. Dry air was obtained from the laboratory compressed air line routed through a desiccant column while humid air was generated by passing air through water held at 30 °C in the humidifier. The water temperature of the humidifier was kept constant by immersing it in a water bath with a thermostat controlled temperature setting (Huggins et al., 2012; Rezaee et al., 2013).

The leaching experiments were initiated with flooded leach on the first day. The samples in the humidity cells were then subjected to weekly cycles involving alternating periods of dry air (3 days), humid air (3 days), followed by leaching with 200 ml of de-ionized water on the seventh day. Each flooded cell was then allowed to sit for a period of 2 hour before draining the leachant into plastic bottles. The two-hour leach time commenced after all of the leachant had been placed in the cell, thus ensuring that the samples were saturated and completely immersed by the leachant water. The valve at the bottom of the humidity cell was then opened and the leachant allowed to drain into the plastic bottles. The volume, pH, and conductivity of the collected leachant solutions were then recorded. At the conclusion of the 7th day, the cycle was repeated. After a number of weekly cycles, the collected leachant waters were combined, based on the variation in pH, and submitted for sulfate concentration, and major and trace elements composition analysis using ICP-OES. The 1st cycle corresponds to the initial aqueous leaching of the rejects conducted prior to the first cycle of exposure to dry and humid air.

The weekly leaching with de-ionized water promoted the removal of products of leachable mineral dissolution produced during the weathering cycle of the previous week. Delivering three-day dry air to the sample partially evaporates the remnant water in the sample pores after the weekly leach without totally drying the sample. As a result, the sample saturation is reduced, air contact is enhanced, and the oxygen diffusion rate through the sample may be enhanced by several orders of magnitude, which promotes the oxidation of constituents such as pyrite. This evaporation also enhances pore water cation/anion concentrations and may also intensify the acidity (e.g. by increasing the hydrogen ion concentration generated from previously oxidized iron sulfide). Increased acid generation will elevate the dissolution of additional sample constituents.

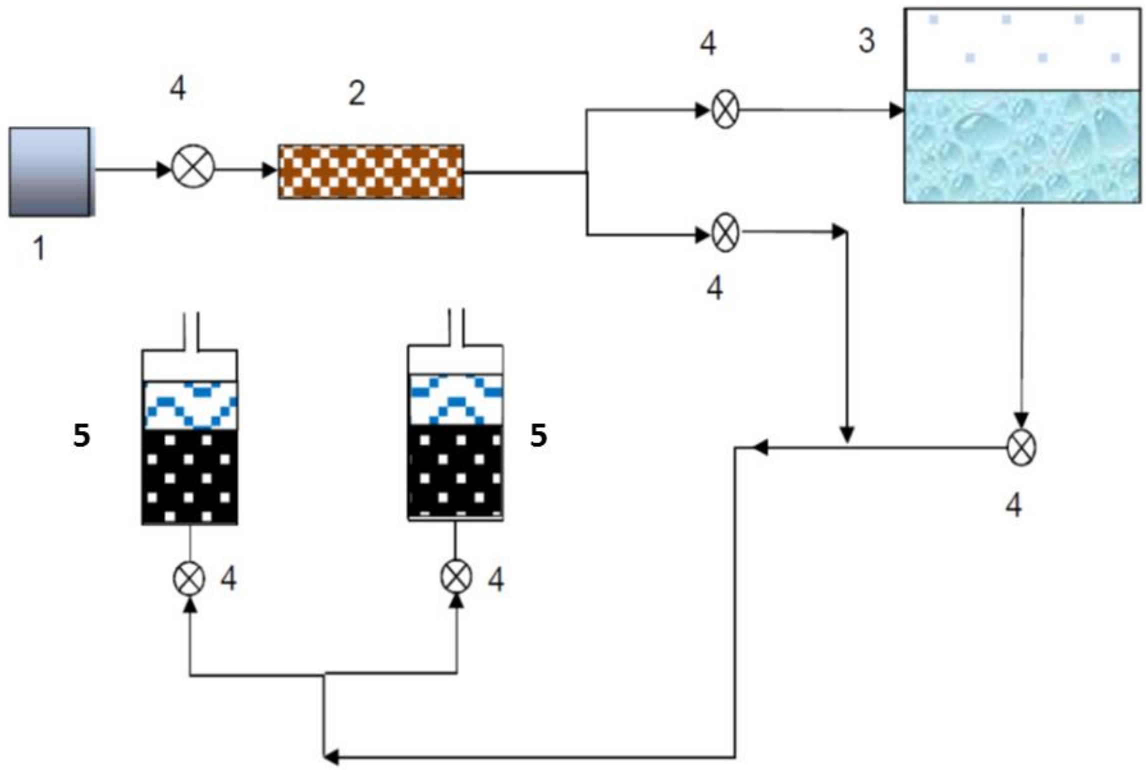


Figure 4.1. Experimental Setup for the dynamic leaching tests based on ASTM method D 5744-96. Numbered Items indicate: (1) Compressed air source, (2) desiccant chamber, (3) humidifier, (4) air-flow control valves, (5) humidity series cells (after huggins et al., 2012).

Continuous evaporation results in over-saturation of water with some mineral phases, thereby causing them to precipitate. The purpose of the three-day wet (saturated) air portion of the cycle is to maintain a relatively constant mass of pore water in the sample for promoting the diffusion of weathering products (e.g, re-dissolved precipitation products) in the residual pore water without totally saturating the sample and adversely affecting oxygen diffusion (ASTM D5744).

4.2.2.2 Static Leaching Experiments

The static or baseline test was setup to run in parallel with the dynamic leaching test. In the static test, 200 grams each of the waste samples were completely submerged under 200 ml of deionized water in a capped glass vessel for the entire period of the experiment. Electrical conductivity and pH of the supernatant liquids in contact with the samples were measured weekly. At the end of the experiment, typically after about 6 months, the solution was drained from the glass vessel and an elemental analysis using ICP-OES was performed on the filtered solution.

4.2.2.3 Analyses of Leachate Solutions

Numerous water samples were obtained during the long-term leaching tests on the coal waste materials. Typically, pH determinations were made on all individual water samples. Determinations of Eh, conductivity, sulfate anion and major and trace element concentrations were also made. However, to reduce analytical costs, some of these determinations were made on combined leachate samples obtained in the dynamic leaching test. Major and trace element concentrations in the leachate samples were determined by inductively coupled plasma with optical emission spectroscopy (ICP-OES), and measurements were made for the conductivity of the solutions and their sulfate ion concentrations were obtained through ion chromatography. Major and trace elements included in the ICP-OES analyses were Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Ni, P, K, Se, Si, Ag, Na, Sr, Tl, Sn, V, and Zn.

4.3 Results and Discussion

Static and kinetic leaching tests were initiated on the coarse refuse and fine refuse samples of three coal waste sources, i.e. high, medium and low pyritic content feedstocks. Frequent measurements of pH were made on the supernatant liquids in the static test and similar measurements as well as electrical conductivity were also conducted on the leach water collected weekly from the kinetic tests.

The pH values of the supernatant liquids in both tests showed a wide range for the different fractions, varying from neutral to relatively acidic, and each remained fairly constant for the entire leaching period (Figure 4.3). The difference in the pH values is due to the difference in mineralogy. The pH value is usually controlled by the acid generating content (pyrite) and natural base content (carbonate and/or exchangeable cations on clay minerals) of the processing waste streams.

Initiation of pyrite oxidation occurs through adsorption of oxygen and water to partly protonated surface of pyrite by bonding to Fe^{2+} (4-1). This reaction releases ferrous iron (Fe^{2+}), sulfate (SO_4^{2-}), and generates acidic condition (H+). Pyrite oxidation also releases chalcophilic and other associated elements into the solution (Moses, 1990; Nordstrom et al., 2000; Dold & Fontboté, 2001; Nordstrom et al., 1979; Nordstrom, 1982; Moses et al.,1987; Fornasiero et al., 1994; Ehrlich, 1996, Rezaee et al., 2013).

$$\mathrm{FeS_2} + 7/2\ \mathrm{O_2} + \mathrm{H_2O} \rightarrow \mathrm{Fe^{2+}} + 2\,\mathrm{SO_4^{2-}} + 2\,\mathrm{H^+} \tag{4.1}$$

High pyrite content of medium and high pyritic total coarse refuse samples therefore result in generating the most acidic condition (pH ~3) in both tests. The lower pH values for these fractions in the dynamic test is due to the fact that the oxidation condition is more aggressive during the dynamic test, where the wet sample is exposed to dry and moist air which favors pyrite oxidation. Generally, pyrite is oxidized at a very low rate, depending on the amount of dissolved oxygen and ferric iron in the supernatant water in saturated static tests. On the contrary, in the dynamic test, the released elements are leached out on a weekly basis while, in the static tests, the released elements including alkali and alkaline elements remain in the container for the entire period of test. Therefore, the availability of such a buffering capability, depending on its amount, may slow down or suppress the pyrite oxidation.

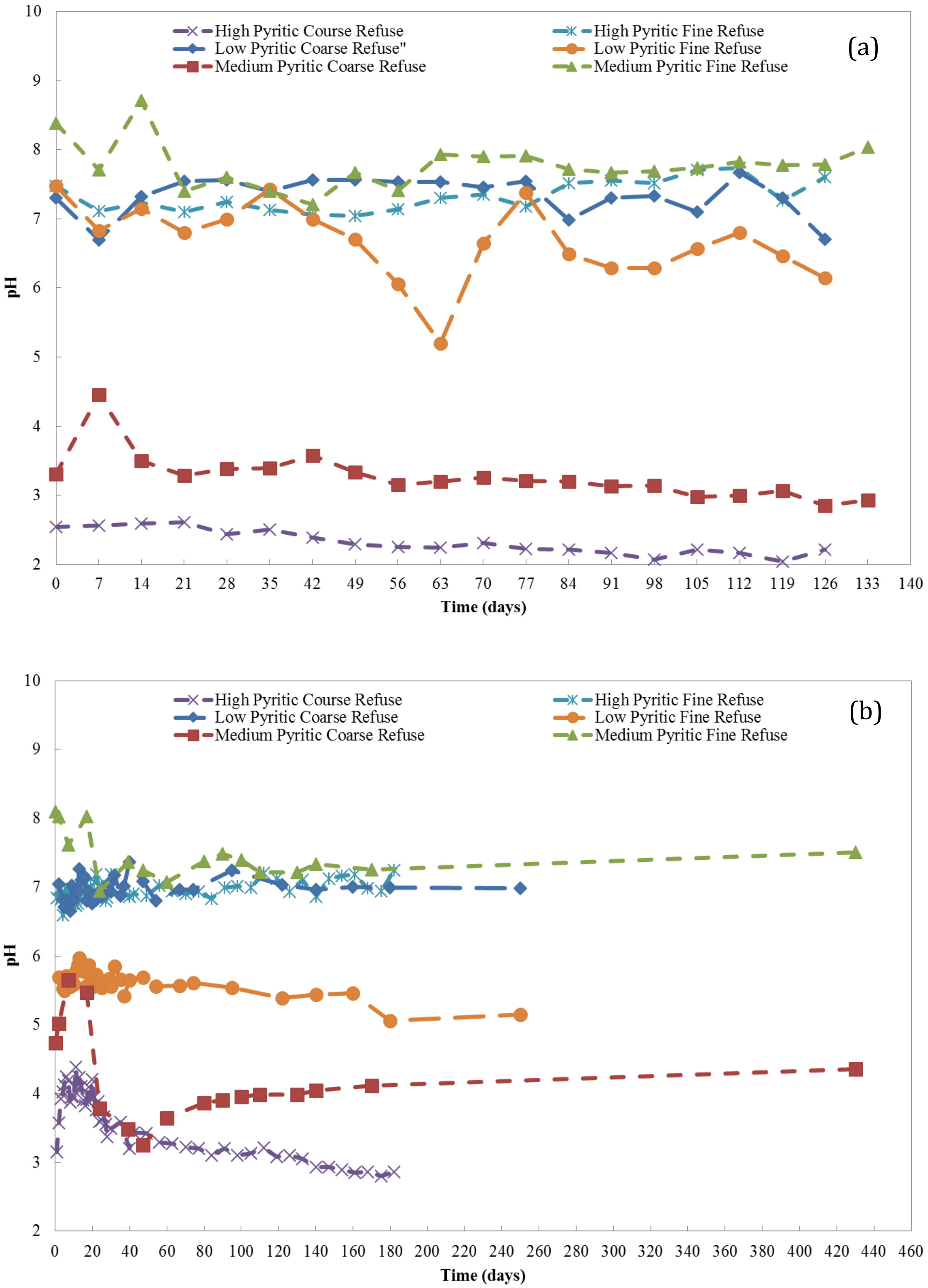


Figure 4.2. pH variation of supernatant liquid in contact with the coal refuse samples in the (a) dynamic and (b) static leaching tests.

Under low pH value conditions such as those associated with the high and medium pyritic coarse refuse samples, ferric iron (Fe^{3+}) produced by ferrous iron oxidation (4-2) would be the primary oxidant while O_2 is the major oxidant at circumneutral pH. Pyrite oxidation with ferric iron (Equations 4-3) is ten times faster than that of oxygen due to the more efficient electron transfer for Fe^{3+} (Ritchie, 1994; Singer and Stumm, 1970; Dold, 2010). The high concentration of Fe in the leachate of these fractions approve the role of ferric iron role in the pyrite oxidation of these fractions (Figure 4.4), as can be implied by Eqs. 4.2 and 4.3:

$$\mathrm{Fe}^{2+} + 1/4\ \mathrm{O}_2 + \mathrm{H}^+ \leftrightarrow \mathrm{Fe}^{3+} + 1/2\ \mathrm{H}_2\mathrm{O} \qquad (4.2)$$

$$\mathrm{FeS}_2 + 14\ \mathrm{Fe}^{3+} + 8\ \mathrm{H}_2\mathrm{O} \rightarrow 15\ \mathrm{Fe}^{2+} + 2\ \mathrm{SO}_4^{2-} + 16\ \mathrm{H}^+ \qquad (4.3)$$

This explains the higher concentration and steeper slope of cumulative sulfate release (as the indicative of pyrite oxidation) for these two samples (Figure 4.4).

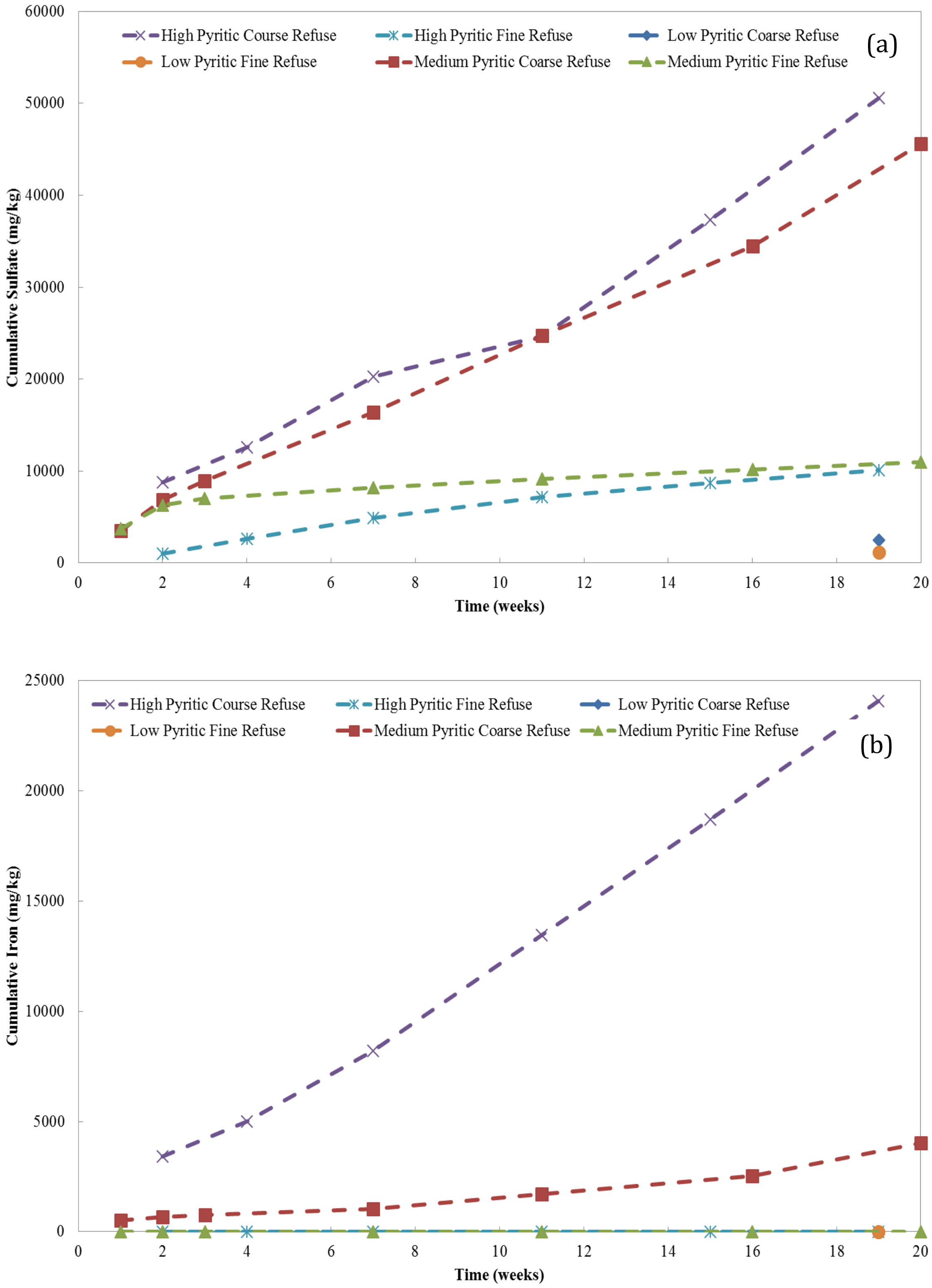


Figure 4.3. Cumulative extraction (mg) of (a) sulfate and (b) iron per 1 kg of material.

The low pH conditions generated by these samples increases the otherwise slow dissolution rate of the clay minerals (as indicated by Al and Si content in Figure 4.5). Dissolution of most clay (aluminosilicate) minerals releases base cation (Fe(II), Ca, Mg), alkali elements such as Na and K, and they contribute in dissolved Al and Si to the tailing pore water as well as H^+ consumption (Blowes & Ptacek, 1994). However, their dissolution rate is much slower than that of carbonate minerals (Jambor and Blowes, 1998). Reactions 4.4 and 4.5 describe the dissolution reactions of kaolinite and illite, respectively, under acidic conditions (Huertas et al., 1998; Köhler et al., 2003; Cama and Ganor, 2015):

$$\mathrm{Al_2Si_2O_5(OH)_4 + 6\ H^+ \leftrightarrow 2\ Al^{3+} + 2\ H_4SiO_4 + H_2O} \qquad (4\text{-}4)$$

$$\mathrm{(Si_{3.55}Al_{0.45})(Al_{1.27}Fe^{(III)}_{0.36}Mg_{0.44})O_{10}(OH)_2(Ca_{0.01}Na_{0.13}K_{0.53}) + 7.80\ H^+ \leftrightarrow}$$
$$\mathrm{3.55\ SiO_2 + 1.72\ Al^{3+} + 0.36\ Fe^{3+} + 0.44\ Mg^{2+} + 0.01\ Ca^{2+} + 0.13\ Na^+ +}$$
$$\mathrm{0.53\ K^+ + 4.90\ H_2O} \qquad (4\text{-}5)$$

Acidic conditions therefore facilitate the mobilization of major and trace elements into the supernatant liquid as shown from the highest concentration of leachate metal for these two fractions compared with others (Figure 4.6). The total content of these fractions is a mixture of major elements and both lithophilic and chalcophilic trace elements (Figure 4.7) since the mobility of metals increases in acidic or alkaline pH (Rezaee et al, 2012). This fact explains the higher electrical conductivity (EC) of the leachate of these two fractions (Figure 4.8). EC of the fine refuse samples was not measured in the static test due to difficulty of such a measurement caused by holding water capacity of the samples.

Note that the higher metal and sulfate concentrations of medium pyritic fine refuse compared to the high pyritic fine refuse in static tests were due to the large difference in the duration of the static tests (180 vs. 480 days).

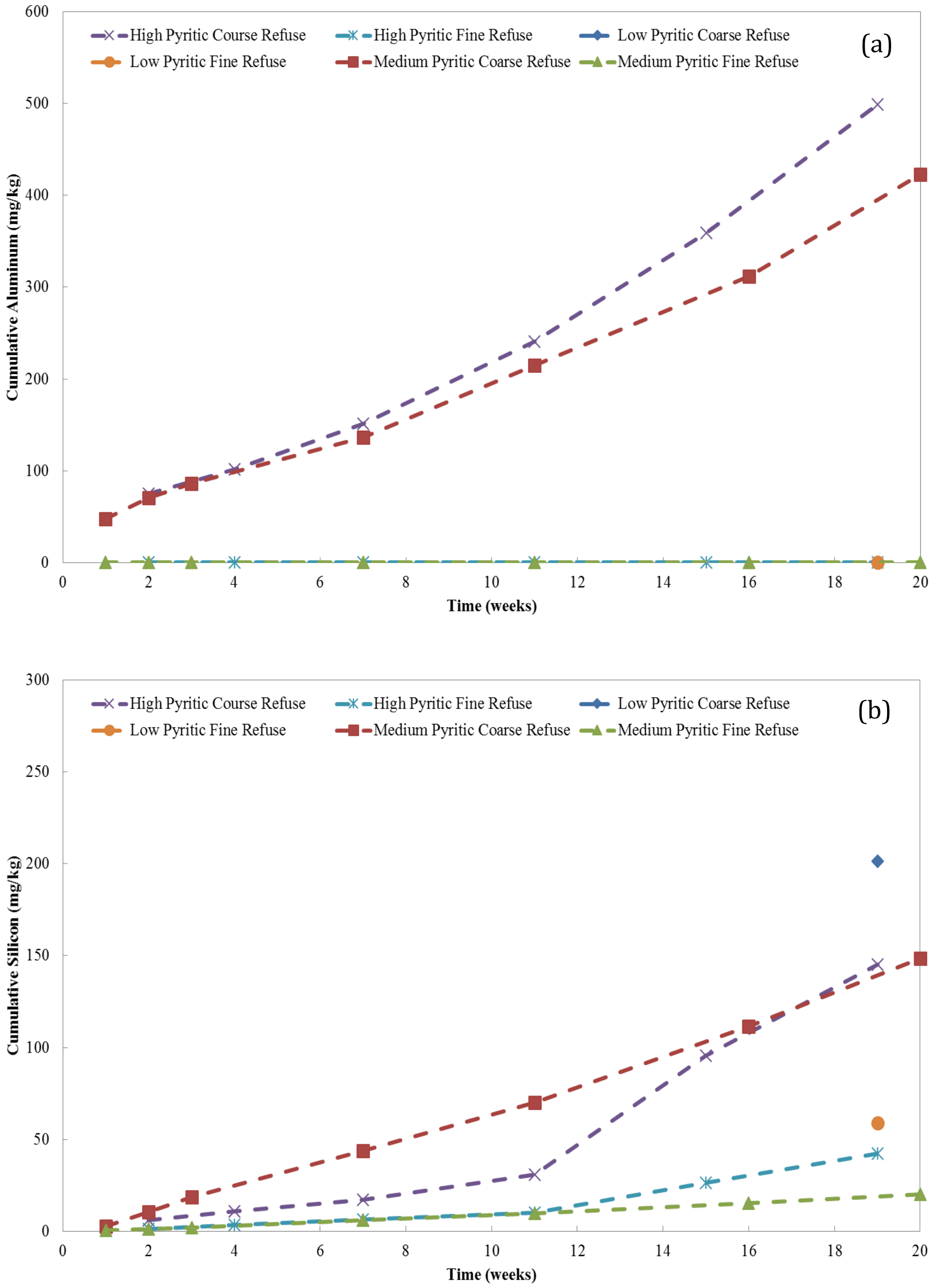


Figure 4.4. Cumulative extraction (mg) of (a) aluminum and (b) silicon per 1 kg of material.

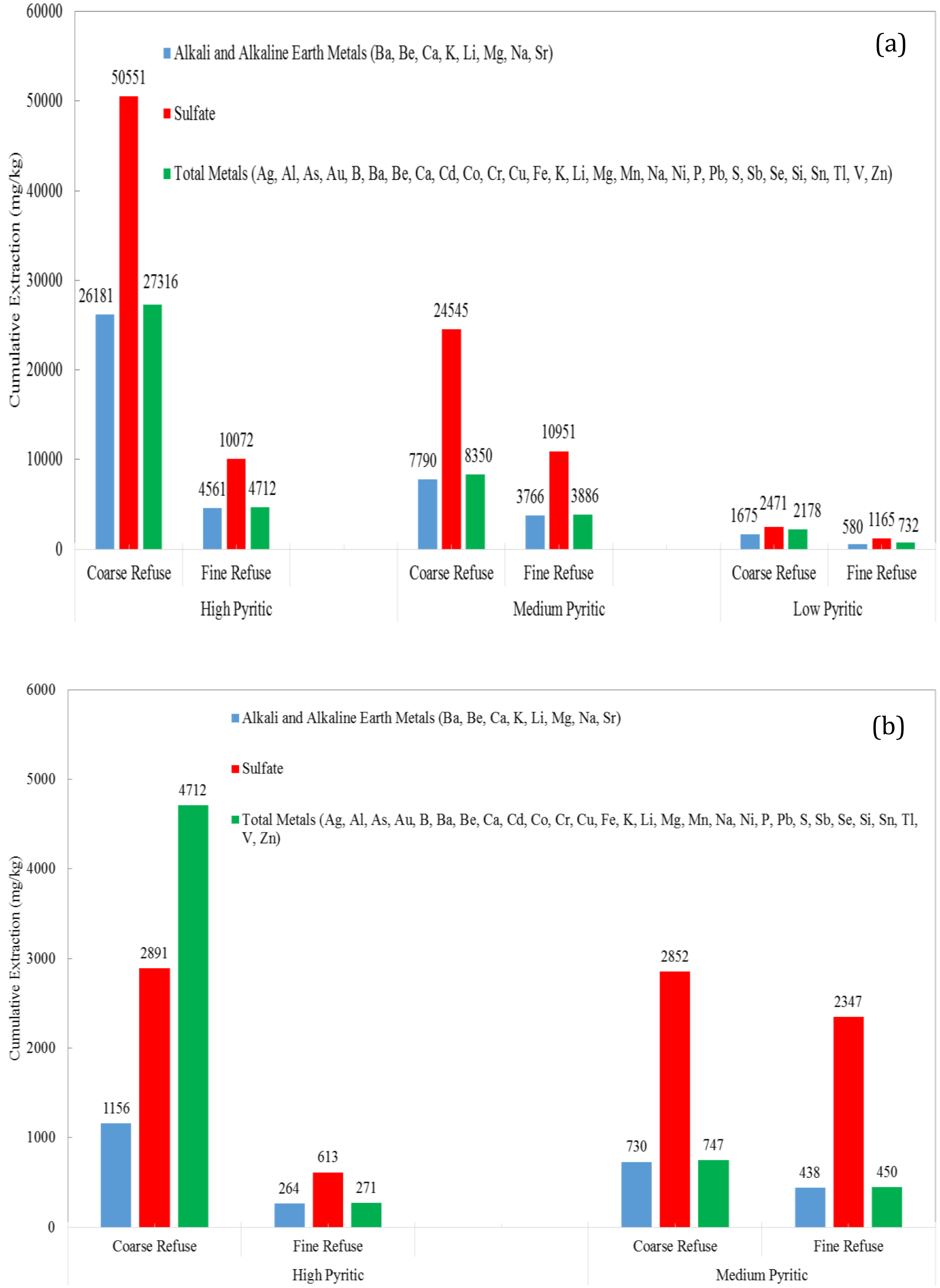


Figure 4.5. Cumulative Extraction of alkali and alkaline earth elements, sulfate and total metals from total coarse refuse and fine refuse sum samples of different coal sources per unit weight of material (kg) in (a) dynamic and (b) static leaching tests.

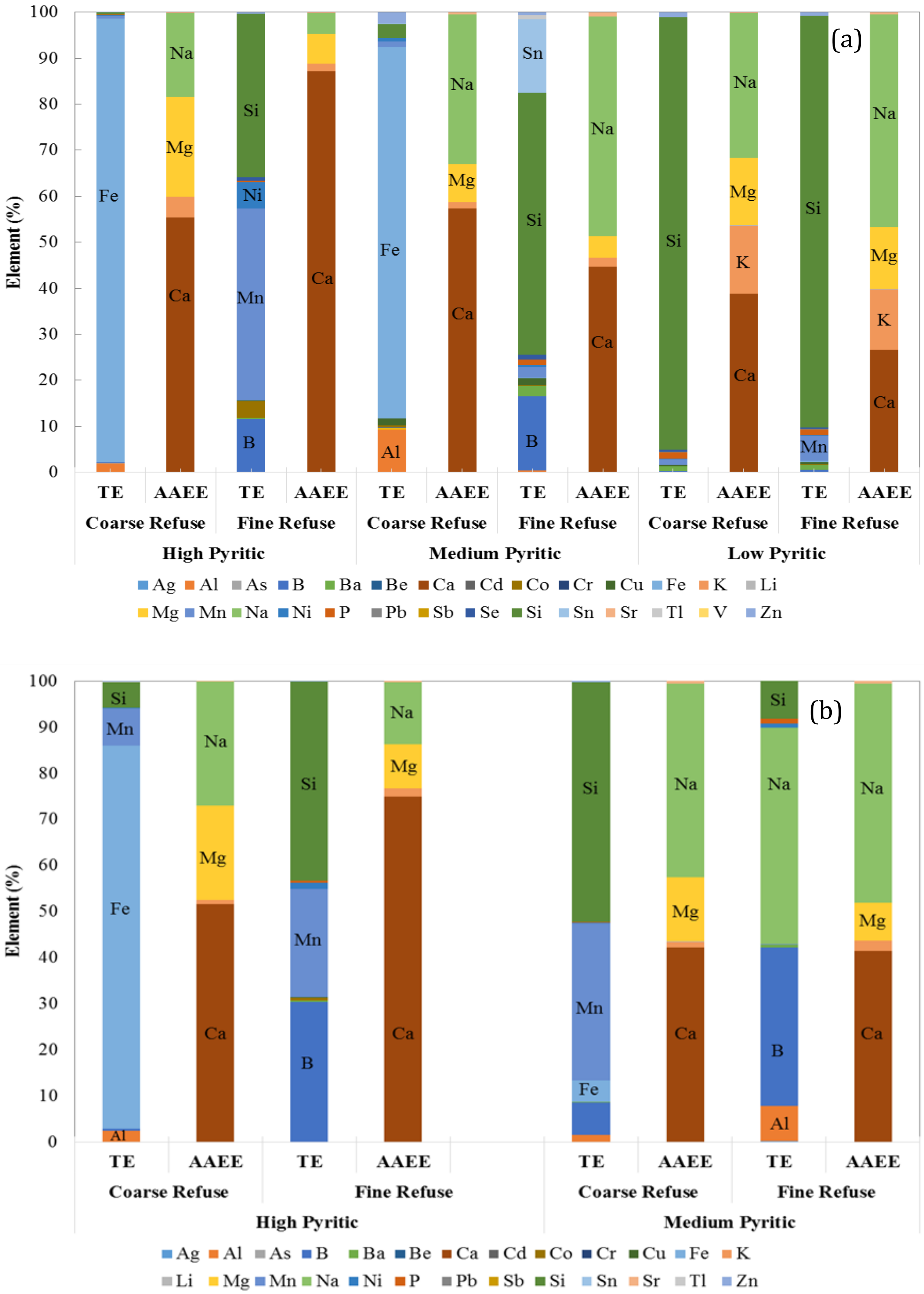


Figure 4.6. Percentage of metal and buffering elements out of total elements (TE) and alkali and alkaline earth elements (AAEE) released from coal waste samples in (a) static and (b) dynamic leaching tests.

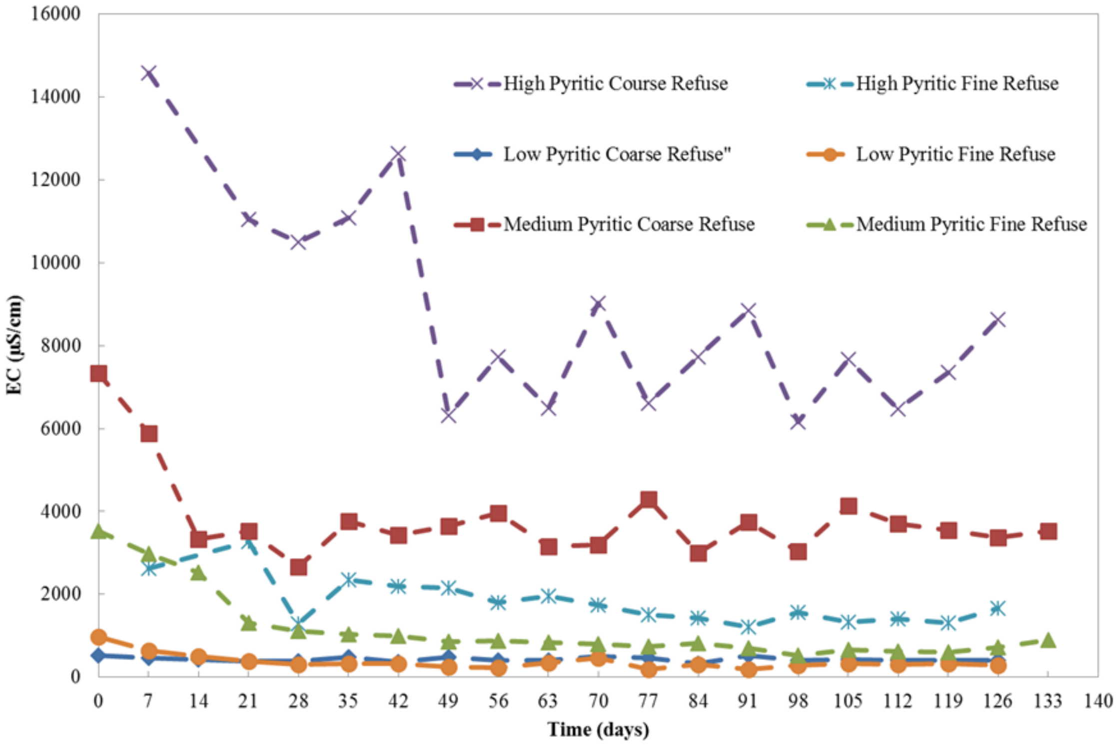


Figure 4.7. Electrical conductivity of weekly leachate of the coal processing plant waste samples in dynamic leaching test.

Existence of readily soluble alkali and alkaline earth elements, e.g. Na and then Ca, as a result of dissolution of carbonate minerals such as calcite and exchangeable base metals on the clay minerals (Plummer et al., 1978; Chou et al., 1989; Wollast, 1990), could buffer the solution and maintain the pH of the leachates close to neutral. This is due to formation of insoluble minerals, such as jarosite and gypsum (4-4 and 4-5) as shown by following reactions:

$$3\ FeS_2 + 3\ H_2O + 13.5\ O_2 + [Na^+]_{sol'n} \rightarrow NaFe_3(SO_4)_2(OH)_6 + 4[SO_4]^{2-}{}_{sol'n} \qquad (4.6)$$

$$[Ca^{2+}]_{sol'n} + [SO_4^{2-}] + 2\ H_2O \rightarrow CaSO_4.2H_2O \qquad (4.7)$$

Therefore, the pH of leachates from lower pyrite content of the fine refuse samples of all three coal sources as well as the total coarse refuse of low pyritic coal sample, compared to the total coarse refuse samples of medium and high pyritic coal sources, was buffered by the calcite content of those fractions, resulting in circumneutral pH of the leachate.

In such circumneutral pH, the oxygen is the dominant oxidant of pyrite which has a low rate, as indicated by the lower contents and slower release of sulfate into the leachate (Figure 4.4). The dominance of oxidation can be observed by a low concentration of Fe in the leachates (Figure 4.4) due to the precipitation of the secondary Fe(III) hydroxides. This precipitation may decrease even the pyrite oxidation rate due to the coating effect of cemented layers (Blowes et al., 1991; Evangelou & Zhang, 1995; Dold et al., 2009). At neutral pH conditions, most of the elements are immobilized, or precipitate as the metal hydroxide. This explain the lower leachate of Fe, and metal content (Figure 4.6 and 4.7), and lower conductivity of the fractions (Figure 4.8).

The pH conditions that were slightly lower than neutral for the low pyritic fine refuse, especially in the static test, is hypothesized to be due to the release of humic acid from the oxidized Coalburg coal (Pawlik et al, 1977).

Comparison of the cumulative amount (mg) of trace elements released from 1 kg of sample to the leachate in the dynamic and static leaching tests (Figure 4.6 and Table 4.5) indicates that the dynamic leaching test is more aggressive than the static leaching test with respect to leaching of most elements from the waste samples. This is due to the limited pyrite oxidation by the dissolved oxygen content of water under saturation conditions. Therefore, storing the samples under water decreases the pyrite oxidation and elemental release rates. The maximum release of the trace elements was related to coarse refuse samples of the high and medium pyritic coal seams when they were subjected to the dynamic leaching test. In this test, pyrite oxidation was enhanced and most of the trace elements were released under the acidic conditions. In contrast, lower amounts of of the trace elements were released under neutral pH condition in fine refuse effluents, suggesting that, for minimizing the mobility of elements, a good strategy would be to keep the pH as close to neutral as possible. Therefore, dewatering of the refuse streams and co-disposing coarse and fine refuse for lower pyritic coal samples provides an efficient way to take advantages of the buffering capability of fine refuse stream to minimize the release of trace elements from coal waste sources. This scenario could be applied for the high pyritic waste streams as well if the pyritic content of the coarse streams is separated and isolated prior to the co-disposal.

The comparison of the dynamic leaching tests reveals the shows that for trace elements especially those elements expected to be associated with pyrite or other sulfide minerals in the coal refuse (viz. chalcophilic elements such as Sb, As, Cd, Co, Fe, Pb, Mn, Ni, Cu, Se and Th) there are huge differences in their apparent mobility in the waste streams of processing of the two coal seams and increases by increase of pyritic content.

In summary, relatively low trace element release and higher pH conditions obtained from fine refuse streams versus the opposite trend for coarse refuse effluent, especially in relation to higher pyritic coal seams, reveals that the acid rock drainage and release of trace elements in the coal waste sources is mainly controlled by the pyritic content of the coarse refuse streams, by which the embankment of the impoundment is built up. This suggest the addition of processing units to separate and isolate the pyritic content of the coarse refuse streams prior to disposal. Such isolation compared to other strategies suggested in this study seems to be the most effective strategy, since it removes the most important element of the acid rock drainage which is pyrite rather than removing water or oxygen out of the reaction (Eq. 4.1).

Table 4.5. Cumulative (mg) of elements released in the leachate from 1kg of the samples calculated based on the ICP measurements for dynamic and static tests.

Elements	High Pyritic				Medium Pyritic				Low Pyritic**	
	Coarse Refuse		Fine Refuse		Coarse Refuse		Fine Refuse*		Coarse Refuse	Fine Refuse
	Dynamic	Static	Dynamic	Static	Dynamic	Static	Dynamic	Static	Dynamic	Dynamic
Ag	0.03	0.00	0.02	0.00	0.35	0.00	0.01	0.00	0.00	0.00
Al	498.71	13.93	0.00	0.00	235.26	0.13	0.33	0.11	0.00	0.00
As	43.43	0.04	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Au	0.00	0.00	0.00	0.00	6.92	0.00	0.00	0.00	0.00	0.00
B	46.76	2.13	8.35	0.63	6.43	0.58	3.91	0.49	0.68	0.35
Ba	0.26	0.02	0.26	0.01	0.18	0.01	0.72	0.01	2.03	0.70
Be	0.20	0.03	0.00	0.00	0.19	0.00	0.00	0.00	0.00	0.00
Ca	1201.11	354.42	4181.23	201.30	3705.60	312.13	2090.92	185.74	761.51	177.38
Cd	0.69	0.01	0.00	0.00	0.15	0.00	0.00	0.00	0.00	0.00
Co	4.38	0.09	1.70	0.01	7.61	0.00	0.04	0.00	0.07	0.09
Cr	5.76	0.11	0.00	0.00	0.54	0.00	0.00	0.00	0.00	0.00
Cu	6.60	0.29	0.13	0.00	47.85	0.00	0.42	0.00	0.68	0.35
Fe	24062.30	475.86	0.10	0.00	2267.17	0.39	0.15	0.00	0.00	0.22
K	160.49	5.68	68.32	5.14	72.66	8.87	88.19	10.24	290.73	87.82
Li	1.69	0.27	0.26	0.03	1.53	0.08	0.52	0.09	1.02	0.17
Mg	528.94	139.92	226.23	25.49	427.18	102.65	192.29	36.59	286.67	89.56
Mn	123.68	45.61	26.45	0.49	26.81	2.82	0.62	0.00	2.71	3.56
Na	381.56	184.80	145.30	36.30	1365.81	310.55	1443.06	210.57	619.36	308.67
Ni	17.41	1.16	2.88	0.03	15.75	0.01	0.07	0.01	0.27	0.09
P	68.61	0.00	0.26	0.01	0.74	0.02	0.23	0.01	2.71	0.78
Pb	0.56	0.03	0.00	0.00	0.89	0.00	0.00	0.00	0.34	0.09
S	18790.25	937.20	3947.82	193.33	8980.29	1043.31	3504.79	751.16	707.36	386.93
Sb	0.91	0.01	0.00	0.00	0.09	0.00	0.01	0.00	0.00	0.00
Se	0.00	0.00	0.38	0.00	0.09	0.00	0.23	0.00	1.02	0.17
Si	145.16	32.08	42.24	0.89	75.75	4.31	20.01	0.74	201.38	58.87
Sn	0.06	0.00	0.00	0.00	4.52	0.00	5.00	0.00	0.00	0.00
Sr	5.27	0.97	7.46	0.66	22.64	4.56	38.83	5.25	4.06	2.96
Tl	0.11	0.07	0.00	0.00	0.09	0.00	0.25	0.00	0.00	0.00
V	0.59	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	11.12	1.04	0.26	0.00	57.08	0.03	0.17	0.05	2.37	0.52
SO4	50550.80	2890.80	10072.44	613.25	24544.61	2851.54	10950.92	2347.05	2470.69	1165.13
TM	27316.39	1258.57	4711.82	270.99	8349.90	747.16	3885.98	449.91	2177.59	732.34

* Higher concentration of the data from this fraction than the fine refuse of high pyritic sample in the static test is due to the longer test duration. ** Static data were not measured for this fractions

4.4 Conclusions

Coal processing plants take advantage of various low cost solid-solid and solid-liquid separation processes for increasing the heating value of coal and/or meeting the market requirements. The upgrading of coal is achieved by rejecting the mineral matter in coal. As a results of such a process, coarse and fine refuse are generated that need to be disposed. In conventional coal disposal, the coarse refuse material is used to build the embankment of the impoundment in which the slurry fine refuse is stored.

Most of the trace elements in coal are associated with minerals, especially pyrite and illite. As a result of coal processing, they are enriched in the waste streams and their potential release to the environment is an environmental concern. To develop sustainable coal waste disposal scenarios, understanding the leaching characteristics of the waste streams is mandatory. Therefore, this research studied the leaching characteristics of coarse and fine refuse streams of three US processing plants treating high, medium and low pyritic bituminous coal seams. Leaching characteristics were studied through conducting dynamic column leaching tests and static tests to simulate the waste disposal conditions.

Characterization of the samples showed the large difference in mineralogy of coarse and fine refuse streams. This variation arises due to the different size distribution of minerals and ways they occur in the coal and processed in coal preparation. Coarse streams contain higher amount of pyrite while fine refuse contain higher amount of clay and calcite, This suggest coarse refuse generates acidic effluent, especially in high and medium pyritic coal, while fine refuse offers buffering capability through dissolution of its calcite content and release of exchangeable metals on the clay mineral. The differences in the mineralogy, therefore, resulted in various leaching characteristics of the samples.

In contact with water, coarse refuse of high and medium pyritic coal generated the most acidic condition (pH~3) for the entire period of the tests, while the pH of supernatant liquids in contact with fine refuse samples and coarse refuse of low pyritic coal were close to neutral. The elements data analysis, suggested that most of the trace elements were released under the acidic pH conditions, in which the pyrite oxidation is also enhanced by the ferrous iron ions in the leachate. Therefore, an effective strategy to minimize the release of trace elements is keep the pH of medium as close as neutral.

The highest amount of release of trace elements were related to the dynamic leaching of coarse refuse streams of high and medium pyritic content, while the least amount of released trace elements were related to low pyritic refuse streams. This suggest that higher pyrite content of the coarse refuse streams is the cause of acid generation and release of trace elements to the effluent. As a result, separation and isolation of high density fraction, i.e. pyrite, of course refuse streams prior to the disposal minimize the environmental impact of coal waste disposal significantly. Subsequent co-disposing of remaining coarse refuse with fine refuse streams then can buffer the supernatant water through the release of self-buffering capability of fine refuse stream. This also can suppress the oxidation of pyrite which is remained in the system due to any efficiency of the separation processes or lower pyritic content of fine refuse streams.

5. MINIMIZING THE ELECTRICAL CONDUCTIVITY LEVEL OF APPALACHIAN COAL WASTE STREAMS EFFLUENT

Summary: Coal cleaning for increasing the heating value or meeting market requirements generates significant amounts of waste materials which are stored in coarse refuse ponds or slurry impoundments. Coarse refuse ponds effluent has shown elevated amount of released trace elements and electrical conductivity (EC). The discharged water of the coal mining to the perennial streams in Appalachia region should have EC below 500 µS/cm. To develop the strategies to minimize the EC of the coal refuse leachates, long term leaching characteristics of the coal refuse streams was studied as a function of material density through conducting column leaching tests, variation of the ASTM standard Test Method D-5744. The results indicated that EC of the refuse streams can be reduced to the 500 µS/cm or greatly decreased depending on the pyritic content of the sample. This high density fractions contain less than %5 of the total material and could be easily separated through manipulating of coal processing plants prior to waste disposal for sustainably coal waste disposal.

5.1 Introduction

Waste generated in coal mining and processing stages are disposed in either coarse refuse pond or fine slurry impoundments. Several alternatives for coal waste impoundments have been proposed. The alternatives include remaining, processing using advanced fine separation technologies and reclamation of coal waste slurry, sending slurry refuse directly for power generation in either conventional boilers or advanced combustion and gasification technologies, surface and underground options such as combined refuse piles, co-disposal fine and coarse refuse, incised ponds or slurry cells, and injection in underground mines (Williams and Kuganathan, 1992; Couch, 1998; Anon, 2002; Wickland et al., 2010; Rezaee et al, 2013). However, there are still practical, technology, efficiency or cost issues related with each alternative.

No matter what method is used for coal waste disposal, addressing related environmental issues such as acid mine drainage, release of trace elements to the environment, conductivity level of discharged supernatant liquid in contact with waste material should be the primary concern.

Pyrite oxidation is the primary sources of acid mine drainage, and causing the supernatant liquid in contact with the solid material to be strongly acidic. In such an acidic condition, major elements, calcophilic and lithophilic trace elements are mobilized. In addition to pyrite, dissolution of carbonate minerals can also enhance the conductivity level of the leachates from the coal mine refuse streams (Streams). Therefore, separation of environmentally concerned fractions in coal processing plants followed by isolation and encapsulation of those fractions could significantly improve sustainability of coal waste disposal.

An in-stream limit of 300 µS/cm has been suggested by the U.S. EPA report EPA/600/R-10/023F to protect 95% of native aquatic macroinvertebrates in the Central Appalachian region, while Cormier et al. (2011) reported a level of 500 µS/cm to substantially disturb aquatic life. To meet the EPA conductivity limit of water, identifying potentially high conductivity producing materials in mine soil overburden and mine and coal processing waste streams, followed by isolation or encapsulation have been suggested to be promising operational methods (Yeheyis et al., 2009; Rezaee et al., 2013).

Short term screen tests on the Appalachian coal waste streams conducted at the University of Kentucky showed less than %10 of material in the waste streams causes high electrical conductivity (EC), as an indicative of the total dissolved solid, of the discharged water from the coal waste disposal. This fraction is the high density fractions of the coarse refuse streams which mostly contain pyrite and calcite. It was therefore suggested if the high density fraction could liberated and separated, the remaining fractions of the coal waste streams could be considered as environmentally benign. Crushing the samples to the top size of 6.35 mm showed relative, not completely, liberation of high density fractions in coarse refuse streams.

In this study, long-term leaching characteristics (pH and electrical conductivity) of the coarse refuse streams as a function of material density is evaluated. The long-term leaching characteristics were studied through conducting column leaching tests on waste streams of two coal processing plants cleaning Appalachian coal seams.

5.2 Experimental

5.2.1 Sample Collection and Preparation

To assess the strategies for minimizing the conductivity level of discharged from coal refuse ponds, comprehensive set of representative samples were first taken at 20 minute time intervals over a 4 hour period from two coal processing plants treating relatively low and high pyritic Appalachian coal seams. The coal seams are:

1. Coalburg, Central Appalachia, WV (low pyritic content)
2. Pittsburgh No.8 coal seam, Northern Appalachia, PA (high pyritic content)

Figure 5.1 illustrates the sampling locations in the coal processing plants. Samples were obtained from following streams: 1) Feed, 2) Clean coal, 3) Dense medium vessel refuse (DMVR), 4) Dense medium cyclone refuse (DMCR), 5) High frequency overflow (HFO), 6) Total coarse refuse (CR), which includes DMVR, DMCR, and HFO, 7) Thickener underflow (TU), and 8) Fine refuse sump (FR), which includes TU and high frequency underflow. All streams were sampled from plant 2, and the samples taken from plant 1 include 5, 6 and 8.

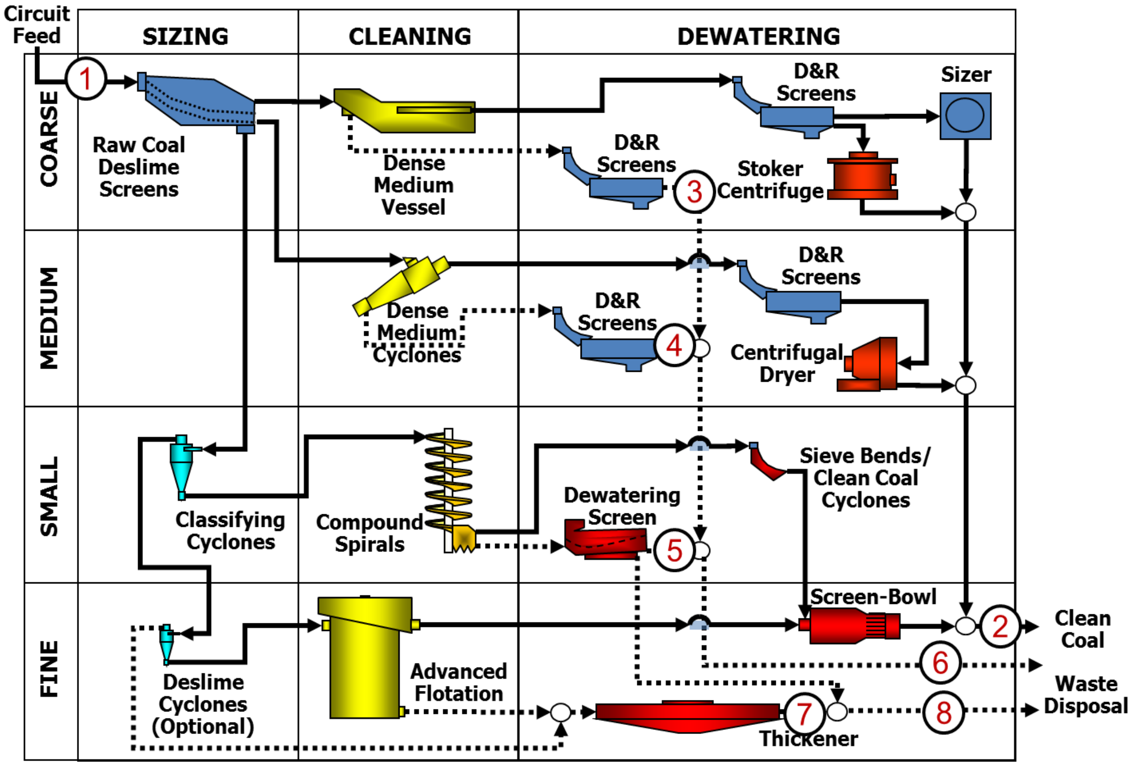


Figure 5.1. Simplified flowsheet for modern coal processing plants and sampling locations.

After sampling, the CR, DMVR, DMCR and HFO samples were spread out and air-dried over a period of about 3 days. CR, DMVR, and DMCR preparation involved crushing the samples to a top size of 12.7 mm (½-inch) using a jaw crusher. The top size was further reduced to 6.35 mm (¼-inch) by crushing in the second stage using a Holmes hammer mill crusher, accompanied by a manual mixing stage to ensure homogeneity of the samples. The coning and quartering method was employed for achieving the reduction in sample volume. The method involved heaping the bulk of the sample in a pile and dividing into four quarters, rejecting two opposite quarters, mixing the two remaining quarters and then repeating the process until a suitable volume of material remained for splitting. A laboratory Jones riffle splitter was employed at this stage for CR, DMVR, DMCR, as well as HFO which finally yielded samples of about 1 kg for analysis and experiments. For splitting, samples were poured onto the top of a riffle which splits the samples into alternating angled slots that discharge into separate containers underneath the riffle. The final samples were stored in sealed bags in a freezer to prevent atmospheric oxidation. The reject portion of the sample was then returned to the barrel and sealed airtight for future use. All the processing, except drying in air, was performed for clean coal. The processes after crushing also were performed on spiral refuse sample.

For the slurry FR and TU sample, the samples were well mixed for 15 min using agitator and several representative slurry samples were taken using Outotec Rotary Slurry Sampler Model WS-220 to evaluate the initial pH, and conductivity and amount of release trace elements into supernatant liquid in contact with the samples, solid percent, and size analysis. The rest of samples were then filtered using pressure filter and dried in low temperature oven for 24 hours. The dried caked samples were then sent to hammer mill crusher with screen size of 1mm, to separate adhered particles from each other. Then splitting and storage steps were repeated for the sample.

The HMVR, HMCR, HFO, and CR samples were subjected to density fractionation to evaluate the long term leaching characteristics of the fractions and identify the fractions that need to be separated and isolated for minimizing the conductivity level of discharged water from refuse ponds.

5.2.2 Sample Characterization

After required preparation, samples were analyzed for ash content, forms of sulfur, major elements using XRF, mineral matter by X-ray Diffraction (XRD) utilizing Rietveld method and elemental analysis by Inductivity Coupled Plasma – Optical Emission Spectroscopy (ICP-OES).

Ash content and forms of sulfur (ASTM D-2492) for the samples obtained from the processing plants are listed in Table 5.1, which indicates that the Coalburg Pittsburg coal seam samples have relatively low and medium sulfur content, while Pittsburgh No.8 coal seam samples have relatively high sulfur content.

Table 5.1. Ash content and forms of sulfur.

Sample	Ash (%)	Forms of Sulfur (%)			
		Total	Sulfate	Pyritic	Organic
Coalburg Coal Seam					
HFO	72.50	0.55	0.01	0.12	0.42
CR	62.30	0.58	0.01	0.31	0.26
FRS	55.50	0.30	<0.01	0.26	0.04
Pittsburgh No.8 Coal Seam					
FEED	22.59	2.84	0.04	1.38	1.42
CLEAN COAL	8.90	3.09	0.03	1.22	1.84
DMVR	86.48	2.19	0.15	1.68	0.36
DMCR	79.86	4.54	0.32	3.53	0.69
HFO	76.04	9.88	0.08	7.79	2.01
CR	81.55	5.29	0.44	4.39	0.46
TU	40.64	1.69	0.22	0.42	1.05
FRS	47.58	3.09	0.26	2.20	0.63

The data indicates that total coarse refuse streams have higher pyritic sulfur content than fine refuse sump sample. The pyritic content data is consistent with Fe content of the sample (Table 5.2). This is due to unliberated pyrite content of dense medium vessel refuse (DMVR) and dense medium cyclone refuse (DMCR), as well as high liberation of pyrite content from high frequency overflow (HFO) stream. The liberated pyrite content in fine fractions (-1 x 0.15mm) is concentrated in the underflow of classifying cyclone and reported to the spiral refuse, and then HFO. On the other hand, ultrafine pyrite particles, which have been reported to the underflow of classifying cyclone due to the water recovery, are also enriched in the spiral refuse and by passing the apertures of high frequency screen may slightly increase the pyrite content of fine refuse sum (FR).

The same explanation can be used to describe the reason for an elevated calcite content in HFO and FR as indicated by calcium oxide contents, Table 5.2. Although the presence of the calcite in the sample may buffer the solution and lessen the release of trace elements and conductivity, this buffering capability may be diluted when this stream is stored with other streams. This dilution ratio is typically around 5, considering typically 80% of run of mine is more than +1 mm, 15 % is between 1 to 0.15 mm and 5% finer than 0.15 mm, and the yield is 70%. As a result of this dilution, the buffering capability decreases and oxidation of pyrite generates an acidic condition and increases the TDS and conductivity (Moses and Herman, 1991; Nordstrom et al., 2000; Dold & Fontboté, 2001; Nicholson et al., 1988, Huggins et al., 2012). It is therefore suggested to treat the coal spiral refuse with mineral spiral to reject high density materials (solubilized calcite and pyrite with high oxidation and dissolution rate) prior to co-disposing with other fractions for partial abatement of the conductivity of aqueous streams. Due to the high pyritic content of the

CR, treating DMV and DMC refuse streams are also suggested to remove the high density fractions and achieve a sustainable coal waste disposal.

The significant variation in the mineralogy of the waste streams arises because of the different size distributions and a difference in the physical occurrence of individual minerals, resulting in their different behavior during coal cleaning. High clay minerals (illite and kaolinite) content of the TU and/or FR, indicated by Al and Si content (Table 5.2), is due to the separation of fine and light clay minerals to the overflow of classifying cyclone which is reported along with fine coal particles either to flotation circuit or directly to thickener.

The higher pyritic contents of CR of medium and high pyritic coal samples indicating low pH, high TDS and conductivity level of supernatant liquid in contact with these streams. On the other hand, circumneutral condition is expected for the low pyritic Coalburg coal waste streams, and FR, and HFO samples with high alkali and alkaline earth elements content.

Table 5.2. Major element analyses (ash basis) of 500˚C ash prepared from the sample.

Sample	% Oxide (ash basis)*											
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	BaO	SrO	SO3
Coalburg Coal Seam												
HFO	61.70	23.44	4.81	0.34	1.06	0.21	3.42	0.09	0.97	0.08	0.02	0.18
CR	62.39	25.98	4.78	0.35	1.18	0.18	3.75	0.12	1.27	0.08	0.02	0.10
FR	60.19	26.73	4.70	0.50	1.32	0.28	4.11	0.10	1.12	0.12	0.03	0.34
Pittsburgh No.8 Coal Seam												
FEED	57.30	21.75	10.18	2.52	0.90	0.91	1.88	0.21	1.23	0.05	0.06	2.74
CLEAN COAL	44.07	21.81	21.13	3.78	0.72	0.64	1.46	0.37	1.05	0.08	0.16	3.27
DMVR	63.73	25.77	4.54	0.67	0.69	0.54	2.08	0.16	1.33	0.04	0.03	0.52
DMCR	59.12	23.98	7.86	1.59	0.74	0.50	1.98	0.17	1.21	0.04	0.03	1.29
HFO	52.45	21.43	15.19	3.69	0.66	0.41	1.78	0.19	1.06	0.04	0.04	0.90
CR	58.96	23.83	9.58	1.53	0.71	0.47	1.91	0.19	1.20	0.04	0.03	1.33
TU	58.06	24.74	3.35	2.74	0.98	2.16	2.12	0.17	1.15	0.05	0.05	3.41
FR	55.49	23.04	9.43	3.98	0.94	1.16	2.01	0.20	1.09	0.05	0.05	2.70

* As %wt. of mineral matter

5.2.3 Leaching Study

Leaching characteristics (pH and EC) of leachates of different density fractions (2.95 sink, cumulative 2.95 float, and cumulative 2.68 float) of HMVR, HMCR, HFO and CR were compared to those of original samples. For size-density fractionation, each sample was first separated to different sizes be sieving. Each size fraction then separated to different density fractions by laboratory float-sink testing using heavy liquids with different specific gravities. The specific gravities (SG) of 2.68, and 2.95 were chosen for density fractionation. These specific gravities were selected to achieve the optimum separations of typical minerals in Appalachian coals, i.e. Specific gravity of 2.68 to float Organic materials, quartz (SG : 2.65), kaolinite (SG : 2.6) and partially illite (SG : 2.6 – 2.9), 2.95 to float the remained illite and also calcite (SG : 2.71), and to sink pyrite (SG : 5 – 5.02). Lithium Metatungstate (LMT) Heavy liquid was used for density fractionation. For density fractionation, the samples first poured in the LMT with 2.95 SG and well mixed manually. Enough time was then given for material to either float or sink. The sink material (2.95 sink fraction) was then well washed and dried for the leaching test, and 2.95 float material was also washed and dried. After getting representative sample from cumulative 2.95 float material for leaching test the sample was subjected for density fractionation at 2.68 float. The Sink and float fractions were washed and dried and representative samples from 2.68 float material was taken for the leaching study. Any required density fractionation is easily achievable by manipulating the coal processing plant in case some fractions are identified for separation and isolation for sustainably disposing coal waste streams. Colum leaching tests as described in the chapter 3 was then conducted on the individual generated fractions as well as original samples. Figure 5.2 demonstrate the laboratory set-up of series of column leaching tests.

Figure 5.2. Column leaching tests set-up

5.3 Results and discussion

5.3.1 Leaching characteristics of origin waste streams

pH and EC of the waste streams leachates were measured on a weekly base (Figures 5.3 and 5.4). Low pyritic waste streams generated the circumneutral pH and low EC in contact with water. Slightly decrease of pH of FR of low pyritic coal may be due to the high release rate of the buffering capability of the sample, and also release of humic acid from such an oxidized coal. Therefore the pH of effluent decreased down to the pH of leachant (D.I water with pH of 5.5).

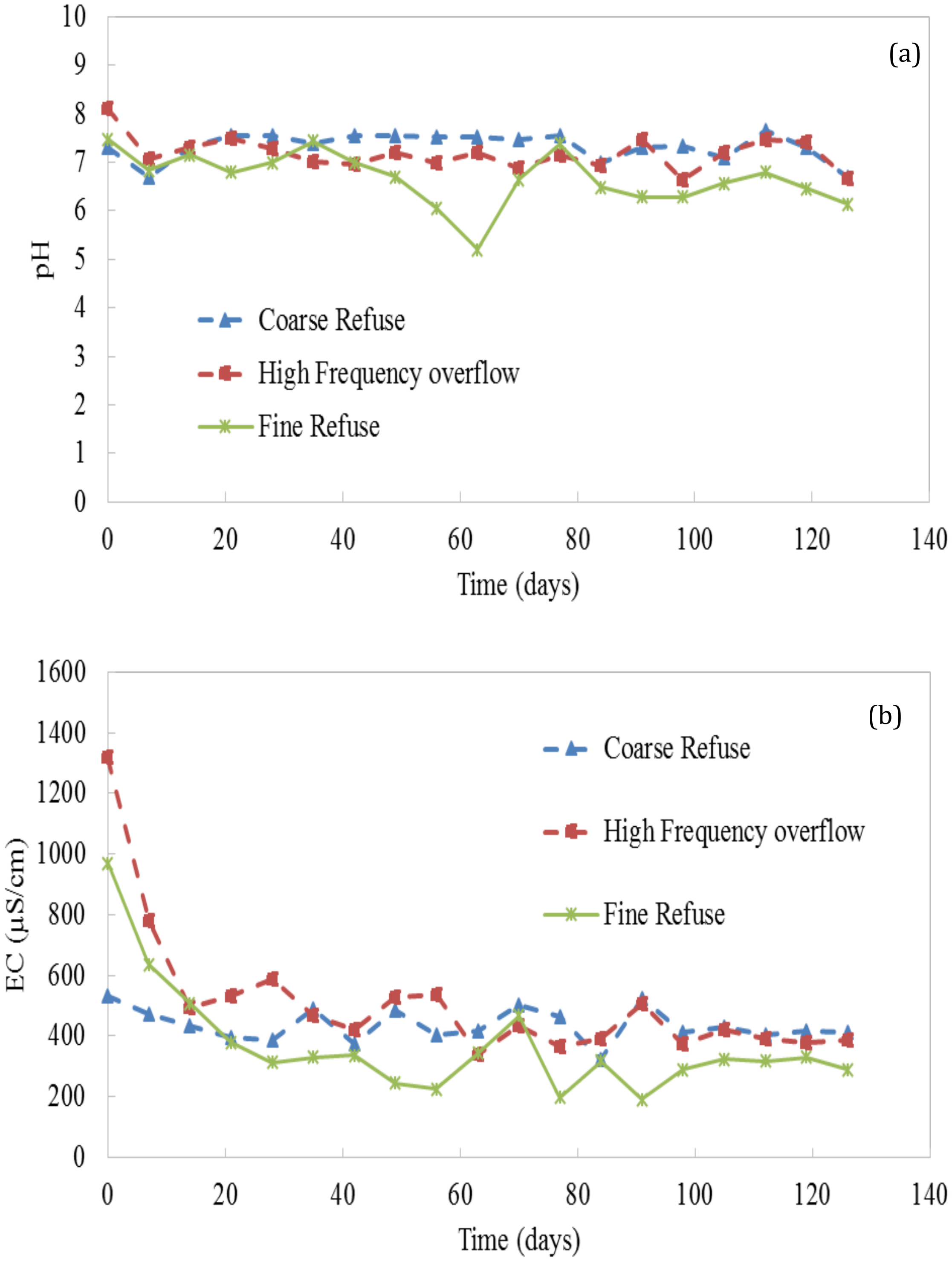


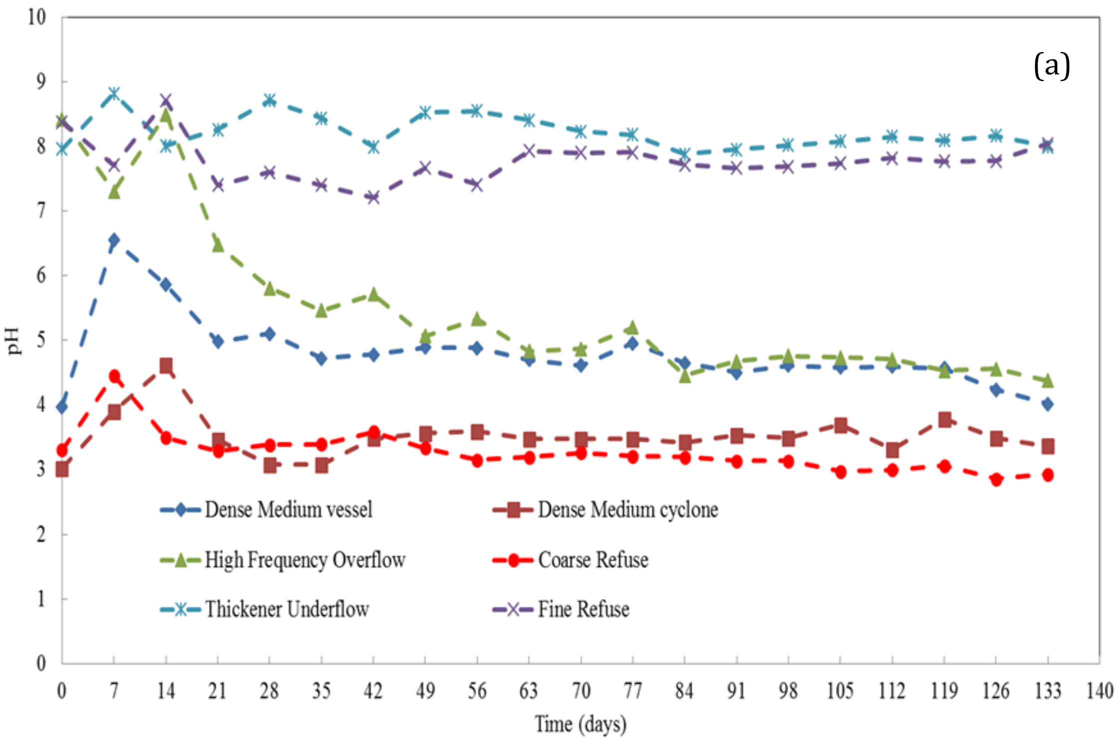
Figure 5.3. Leaching characteristics of low pyritic coal refuse streams (a) pH and (b) EC

Thickener underflow and fine refuse sump samples of high pyritic coal seam demonstrated pH of close to neutral during entire period of tests due to lower pyritic content and their self-buffering capability. Fine refuse sump sample of medium pyritic coal, showed slightly lower pH and higher EC than thickener underflow sample, which shows the effect of addition of high frequency underflow to fine refuse streams, and it is suggested that high frequency underflow is treated with multi gravity separation (MGS) prior to addition to fine refuse stream. This treatment may even further decrease the EC supernatant water in contact with the fine refuse stream in coal waste impoundment.

High frequency samples that contain high calcite and pyrite concentration (Tables 5.1 and 5.2) generated alkaline pH at the first several weeks due to the rapid dissolution of calcite. By decreasing the buffering capability after several weeks its pH drops to 5 and remained weekly acidic in entire period of the test. Dense medium vessel refuse of medium pyritic coal seam, with low pyritic and low calcite content also showed slightly acidic condition. However, dense medium cyclone refuse with relatively high pyrite and low calcite content caused acidic pH of its supernatant liquid. The same behavior was observed for the coarse refuse.

Comparison of EC of all the waste streams samples from the plant treating high pyritic coal seam, revealed that total coarse refuse stream has higher EC than all of its sub-streams. This is due to the fact that the addition of the high frequency to dense medium vessel and dense medium cyclone, increases the pyrite content while its related calcite content is diluted. This also explain the very acidic condition of total coarse refuse stream. The high conductivity of the coarse refuse streams is mostly being driven with high acidity and EC of dense medium cyclone, and subsequently with the high frequency overflow (Figure 5.3).

As a result of these analysis, it is suggested that coarse refuse sub streams are treated to separate the high density fractions which is mostly contain pyrite and calcite to decrease the EC of the water breached from embankment prior to discharge of refuse pond water to water streams.



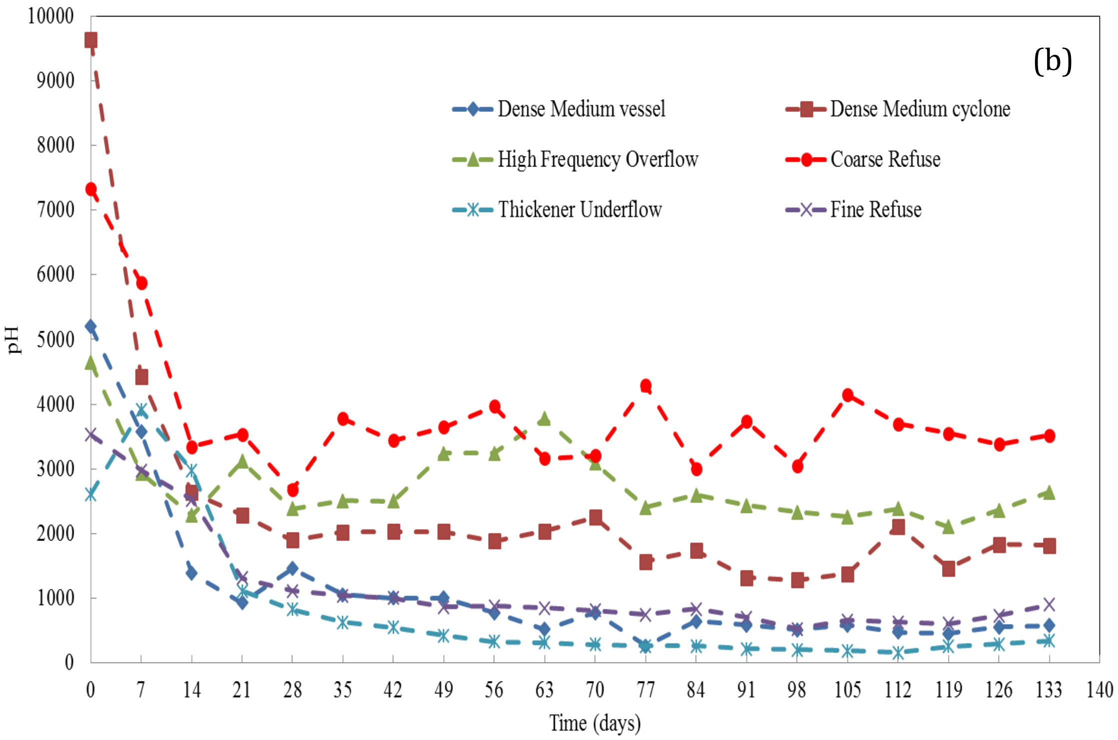
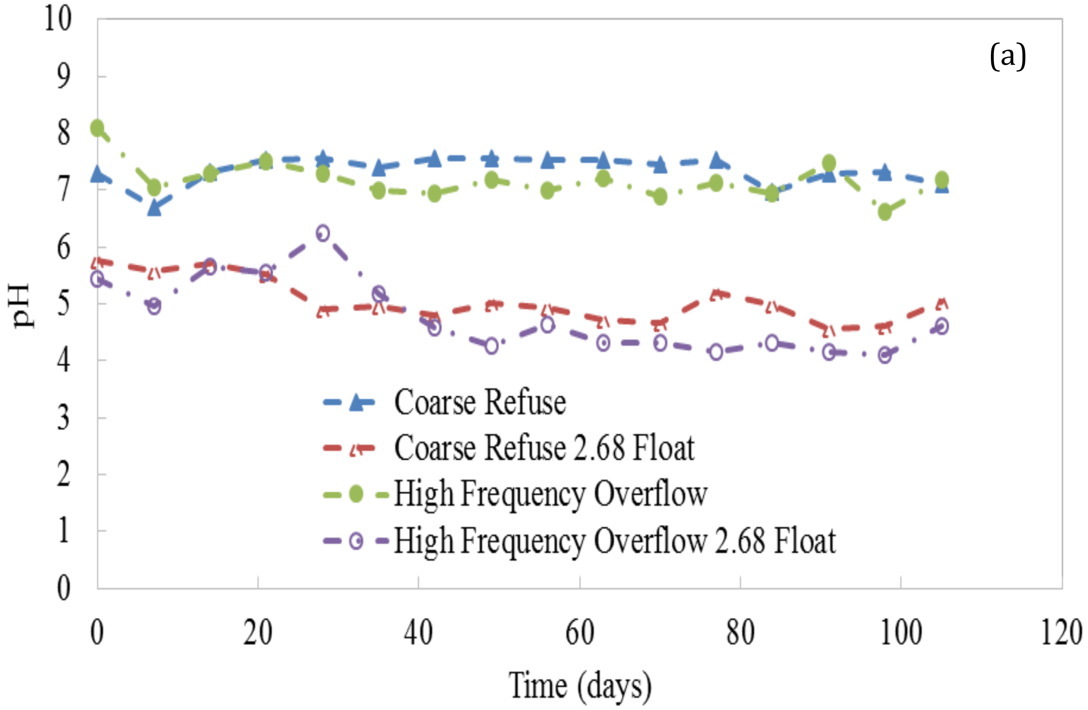


Figure 5.4. Leaching characteristics of high pyritic coal refuse streams (a) pH and (b) EC Leaching characteristic of refuse streams as a function of material properties.

5.3.1.1 Low pyritic coal refuse streams

For low pyritic waste streams, 2.95 sink and 2.95 float material (mostly pyrite, calcite and partially illite) were removed from coarse refuse and high frequency overflow samples and leaching characteristics of 2.68 float material were compared to those of original samples. The removed fractions from coarse refuse and high frequency overflow contain only 1.6 and 1.7 percent, respectively, of the total samples. The comparison of pH of leachates from 2.6 float material with the original samples (Figures) showed by removing less than 2% of the materials from those waste streams, the pH of the solution remains almost constant and close to the pH of deionized water (5.50) which was used as the leachant in the column leaching test. The EC of leachates were also remained below 500 µS/cm for the entire period of the experiments. The EC o the fine refuse is below 500 µS/cm except the first few weeks. Higher EC of the first few weeks of this fraction is due to the oxidation of the surface of the sample during filtration and oven drying, which is not the case for the mining practice. This indicate that crushing to coarse refuse sample to 6.35 mm, rejecting 2.68 sink fraction (1.6% by weight), and removing the magnetic fraction of fine refuse streams (1.6% by weight) assures the effluent of waste streams could be discharged without any chemical or physical water treatment.



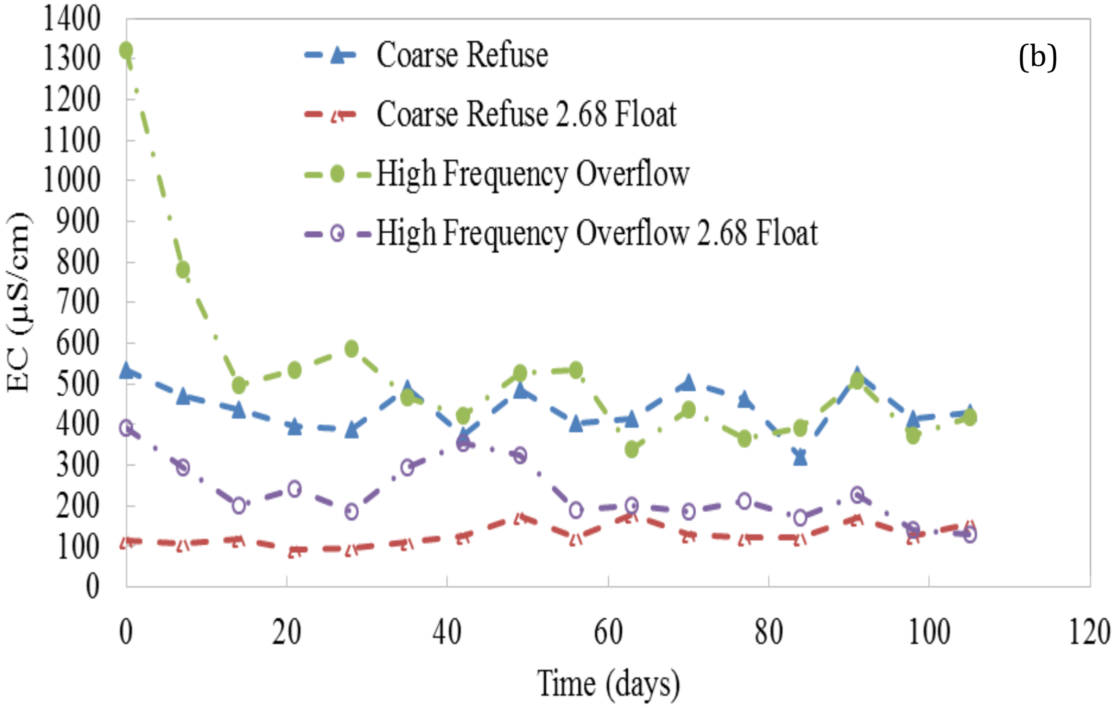


Figure 5.5. (a) pH and (b) EC of supernatant liquid in contact with low pyritic coal refuse samples.

5.3.1.2 High pyritic coal refuse streams

Colum leaching tests were performed to evaluate the leaching characteristics of density fractionated samples (2.95 sink, cumulative 2.95 float, and cumulative 2.68 float) of high pyritic coarse refuse and its associated sub-streams, i.e. DMVR, DMCR and HFO (Figures 5.6 to 5.8). For all the fractions 2.95 sink showed significantly higher EC than the rest fractions as well as original samples. Isolating that fraction resulted in %62 reduction of the EC of the coarse refuse stream which is due to the rejecting mostly pyrite from the sample. Additional isolation of 2.95 float, which is expected to be mostly calcite and partially illite, resulted in additional %6 reduction in the EC. Although the second stage reduction in EC is not significant as first stage, since even very small reduction in EC result in reduction of physical or chemical treatment and also the processing cost is typically less for achieving lower cut-densities in processing plants, it is suggested to separate and isolate 2.68 float materials from the coarse refuse streams.

Comparison of the results for different sub-streams indicates that higher reduction in EC after isolating 2.95 sink and 2.95 float occurs in the high frequency overflow. This is due to the lower size distribution of this fraction (0.15 to 1mm) and the minerals are relatively liberated in this streams, resulting in more efficient separation of minerals into different density fractions.

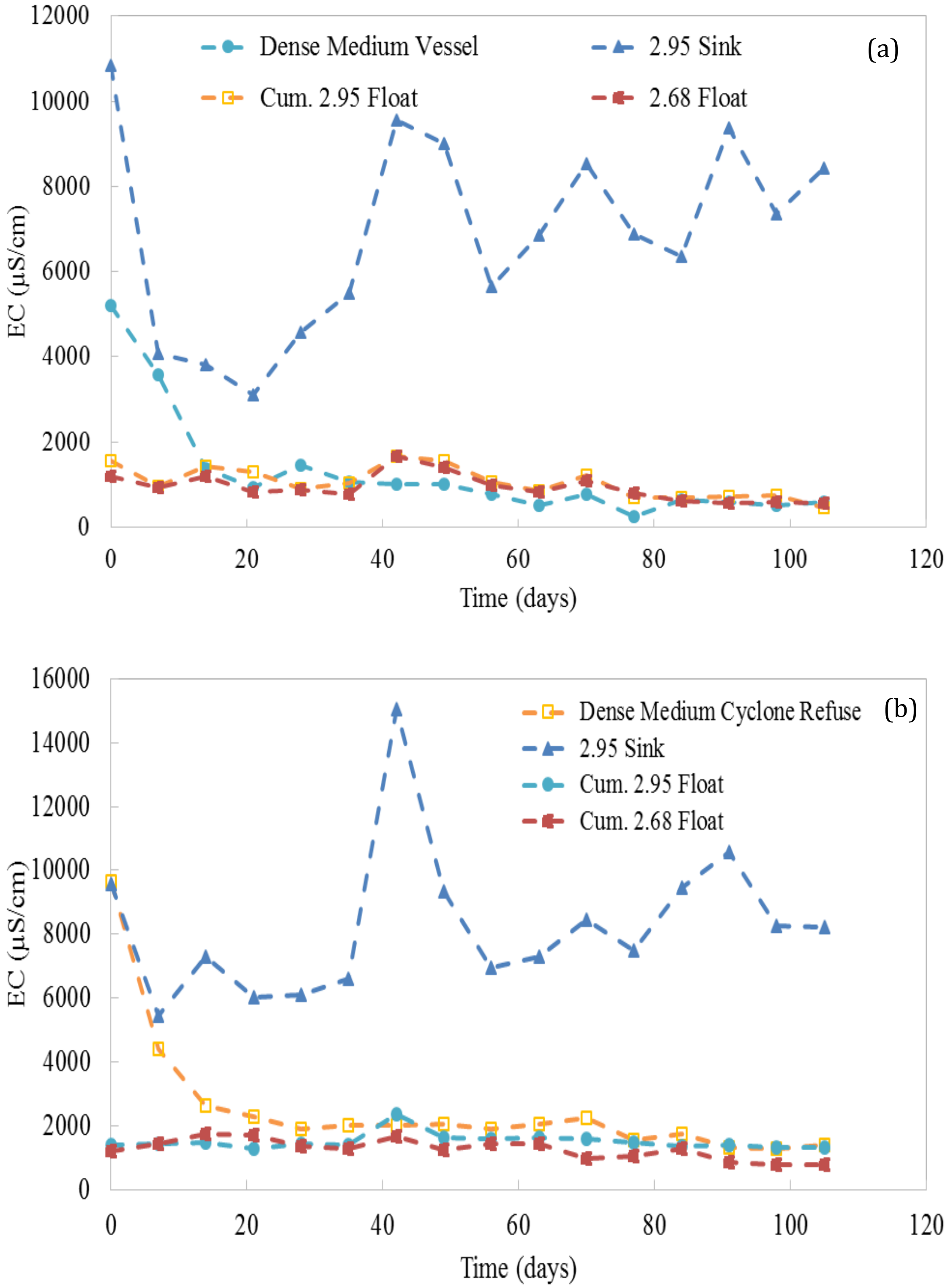


Figure 5.6. EC of supernatant liquids in contact with original and different density fractionated samples of (a) dense medium vessel and (b) dense medium cyclone refuse streams.

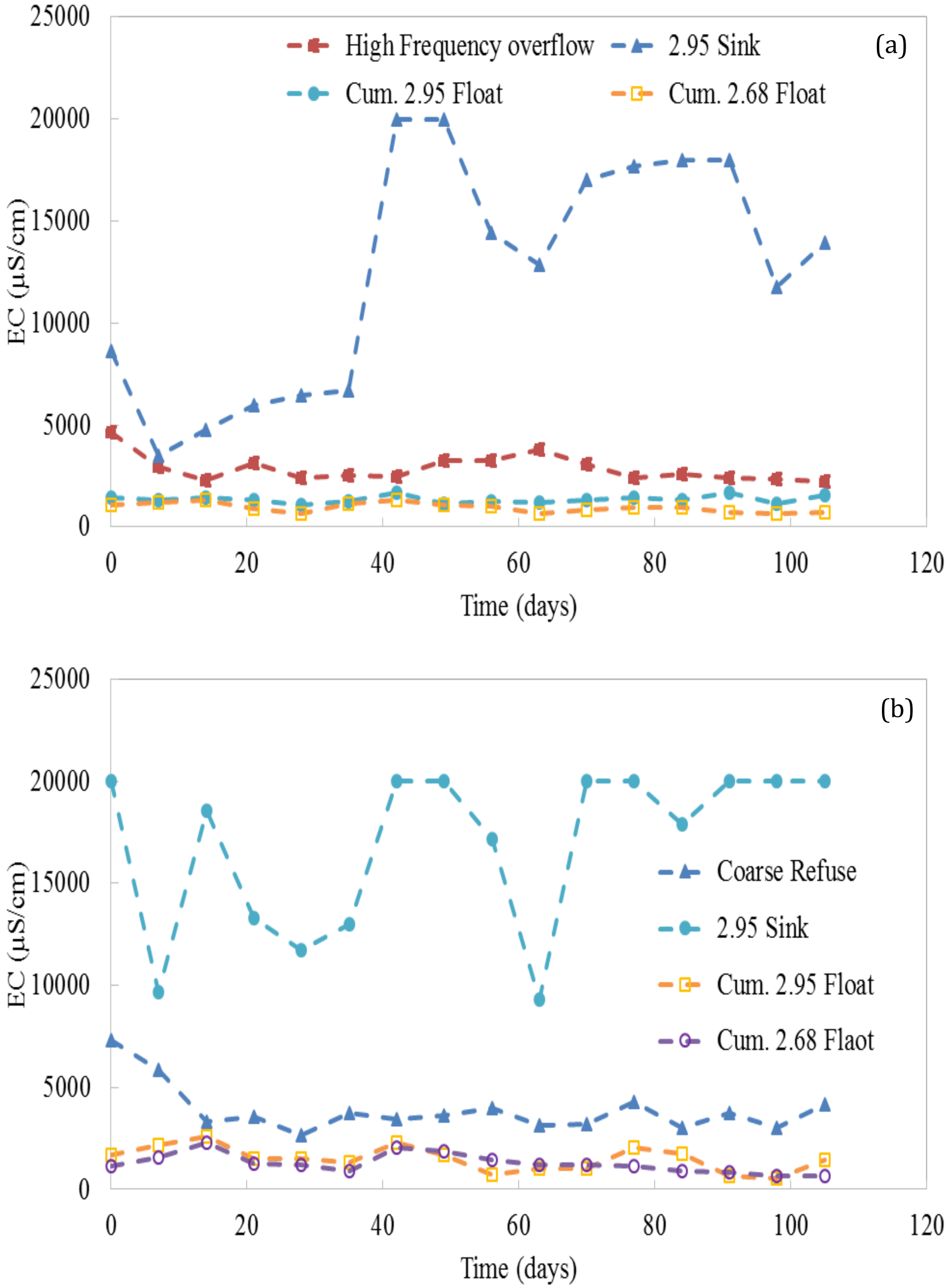


Figure 5.7. Figure 5.6. EC of supernatant liquids in contact with original and different density fractionated samples of (a) high frequency overflow and (b) coarse refuse streams.

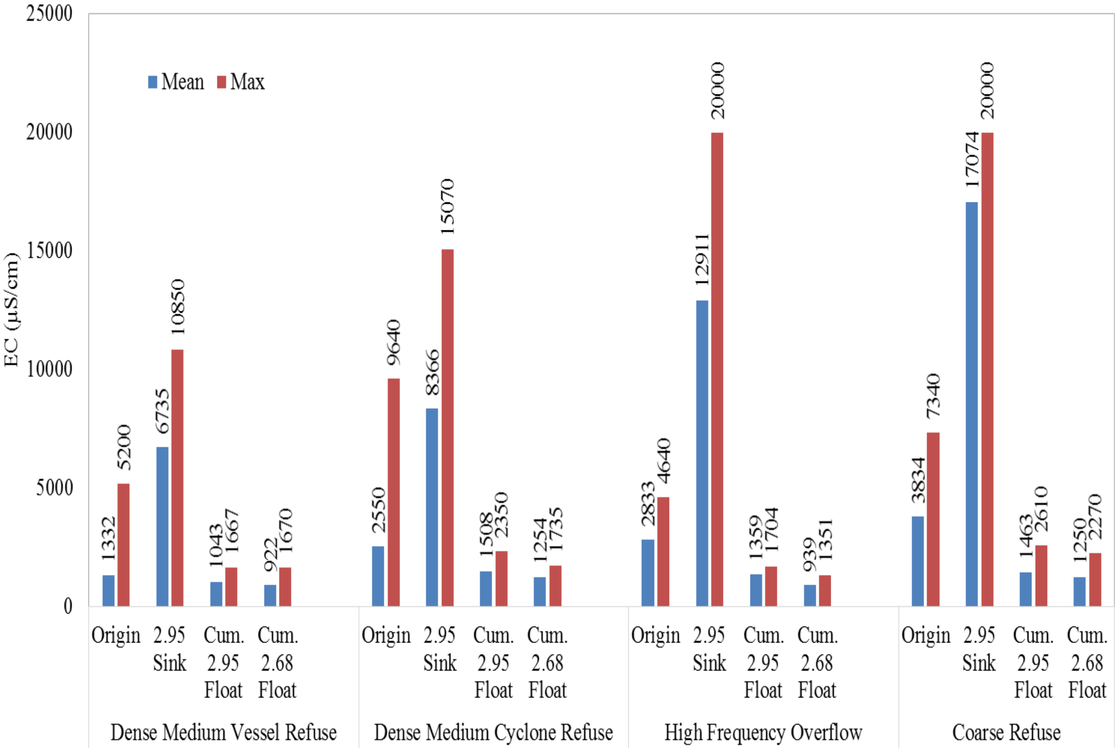


Figure 5.8. Figure 5.6. Average and maximum EC of supernatant liquids in contact with original and different density fractionated samples of high pyritic refuse streams.

The high pyritic processing plants capacity is 1600 (tph). The mass yield (mass percentage of the plant feed reporting to the clean coal product stream) of the plant is %78. Out of 1600 (tph) feed, 1244 (tph) is reported to the clean coal stream, 258 (tph) to coarse refuse and 98 (tph) to the fine refuse streams. In Coarse refuse streams, 40 and 54 percent are reported from dense medium vessel and dense medium cyclone separation units, respectively, and the remaining %6 material is reporting to the coarse refuse streams through high frequency over flow. Table shows the weight percentages of the density fraction of the coarse refuse stream and its sub-streams, indicating isolating only less than %5 of materials (2.95 sink and 2.95 float) in the coarse refuse stream, results in %69 reduction of max EC and %67 reduction of average EC of the leachate from refuse ponds.

Table 5.3. Size distribution of the density fraction of high pyritic refuse streams.

Sample	2.68 Float	2.95 Float	2.95 Sink
DMVR	95.74	96.17	3.83
DMCR	95.74	96.17	3.83
HFO	84.47	86.43	13.57
CR	95.04	95.57	4.43

The results is in consistent with the conductivity screening-level (CSL) test, and shows the efficiency of the short CSL test for identifying high generating conductivity fractions that need to be separated and isolated.

For further decrease of EC it is suggested that DMVR and DMCR crushed to finer top size (1mm) for more liberation of high density materials and more efficient separation of those fractions followed by isolation.

Based on the data provided by conducting long term leaching characteristics, the following modification could be applied for the coal processing plants for mineral segregation in waste streams to minimize the release of trace elements:

1- Addition of mineral spiral to the fine (0.15 to 1mm) circuit for rejecting high density fractions
2- Crushing DMVR and DMCR streams to top size of 6.35 for liberating high density materials

3- Addition of gravity separator units such as jig for separation of liberated high density fractions

4- An alternative for the second and third stages would be crushing the samples to 1mm top size and rejecting the high density fraction through mineral spirals (further economic and geotechnical analysis is suggested to be performed for evaluation of the alternative).

5.4 Conclusions

Waste material generated in coal processing plants are disposed in coal refuse impoundments and refuse ponds. Mineral oxidation and dissolution in the waste may cause environmental issues especially regarding to mitigation of trace elements and possibly increasing total dissolved solids and conductivity level of water streams.

In order to develop strategies to minimize the conductivity level of discharged water from refuse ponds, long term leaching characteristics of refuse streams from processing plants treating low and high pyritic Appalachian coal seams were first examined as a function of density. The long term leaching studies were conducted through column leaching experiments.

The results showed that removing 2.68 material from coarse refuse of low pyritic coal which contains %1.6 of the waste material, results in reduction of conductivity level of leachate below 500 µS/cm, the limit of conductivity level Appalachian perennial streams.

For the high pyritic coarse refuse sample, excluding 2.95 sink material which contains %4.4 of the total refuse material decreased the average EC of the leachates from 3834 µS/cm to 1250 µS/cm (%62 reduction). Additional exclusion of 2.95 float material which is only 0.5% of the total materials, resulted in further %6 reduction of EC and the leachate of the average of EC of remaining material (2.68 float fraction) was 1250 µS/cm. This significant reduction of EC of the leachate could significantly reduce downstream physical or chemical treatment of the leachate prior to discharge.

Comparison of the EC results from separation of high density fraction from sub-streams of coarse refuse stream suggested that the EC of the leachate can even further decrease if material is crushed to finer top size (1mm). This size reduction causes more liberation and higher efficient separation of the high generating EC fractions.

The density separation required for separation and isolation of high density material in refuse streams can be easily achieved by manipulating the coal processing plants for treating the refuse material prior to disposal. This study suggests addition of mineral spirals to fine circuit for treating spiral refuse stream, crushing the coarse and medium circuits (dense medium vessel and dense medium cyclone) to top size of 6.35 and rejecting high density fractions through dense medium cyclone units.

6. CONCLUSIONS AND FUTURE WORK

The research objectives and tasks stated in the chapter 1 were successfully performed and the major research findings and recommendations for future research are summarized in this chapter.

6.1 Conclusions

Coal processing plants take advantage of various low cost solid-solid and solid-liquid separation processes for increasing the heating value of coal and/or meeting the market specifications. The upgrading of coal is achieved by rejecting the mineral matter in coal, thereby generating coarse and fine refuse materials as byproducts. Waste material generated in coal processing plants are disposed in engineered refuse piles and refuse impoundments or ponds. Oxidation and dissolution of enriched mineral content of the coal waste streams may cause environmental issues especially with regards to mitigation of trace elements and possibly increasing total dissolved solids and electrical conductivity (EC) level of water streams.

The main objective of the work described in the dissertation was to develop strategies to minimize the environmental impacts of coal refuse disposal. A comprehensive literature survey suggested a fundamental knowledge and practical operation gap between the current status and desirable sustainable coal waste disposal. Therefore, a thorough fundamental investigation of short-term and long-term leaching characteristics of coal waste streams and identification of sources for environmental contamination by current status of coal waste disposal was conducted in this work. In addition, experiments conducted to specifically identify the environmental issues as a function of material properties that can be exploited for separation such as particle size and density and the modification of coal processing plants for more sustainable coal waste disposal were suggested. Major conclusions and contributions were derived from the research:

1- Understanding the effect of parameters on conductivity is necessary for developing a quick and inexpensive test for conductivity screening-level. The research studied the effect of surface area, volume-to-surface area ratio, and the amount of oxidant on the electrical conductivity of the leachate generated from contacting with coal refuse. The results of a parametric study based on a 3-level Box-Behnken design were used to develop empirical models for predicting the conductivity as a function of the aforementioned parameters. Separate models were developed for two particle size fractions and two density fractions to assess the impact of mineral composition on conductivity.

2- Based on the model results, the order of significance on electrical conductivity was: Volume-to-surface area ratio >> amount of oxidant ≈ interaction effect of oxidant and volume to surface area ratio > interaction effect of volume-to-surface area ratio and surface area. The independent effect of surface area was not significant in all the models.

3- Based on these results, a standard test was developed for conductivity screening-level test (CSLT) which involved the following steps: i) particle size analysis by sieving, ii) particle density measurement, surface area calculation using equation 2.1., iii) the addition of a given volume of water to the solid sample in an amount that provides a 1:1 ratio for volume-to-surface area, iv) agitation of the water and solid mixtures contained in a capped container for 15 min, and v) measurement of electrical conductivity after allowing time for particle settling. This procedure can be applied for conductivity screening-level assessment of various waste stream types.

4- The conductivity screening-level tests were utilized to quantify the electrical conductivity (EC) as a function of material properties such as mineralogy, particle size and density, which could be used to identify environmental sensitive fractions that require separation and isolation to remedy environmental concerns. The results showed that the EC of leachate derived from coarse refuse streams are much higher than fine refuse streams. Based on the conductivity screening-level tests where the same leachant water-to-surface area ratio of 1:1, the order of electrical conductivity from highest to lowest was: dense medium vessel reject > dense medium cyclone reject > high frequency overflow > fine reject stream > thickener underflow.

5- The results of CSLT indicated that less than 5% of material in the coal refuse is the primary source of the environmental issues associated with elevated total dissolved solids level of supernatant liquids in contact with coal processing waste streams, as indicated by high EC level in the water discharged from coal processing waste streams. The high generating EC fractions appear in the highest density fractions (SG > 2.68). Liberation and separation followed by isolation of this fraction results in significant reduction of EC in the discharged water from coal processing waste streams.

6- Characterization of the coal refuse streams showed a significance variance in mineralogy between the coal waste streams. As a result of processing, coarse refuse streams are enriched in pyrite and therefore have higher acid generating potential than fine refuse Furthermore, fine refuse streams are enriched in clay minerals and calcite and therefore have natural-buffering capability. The variation in the mineralogy between waste streams in a given coal processing plant arises due to the differences in particle size and density distributions between the various mineral types, which effects their movement into the various process streams of a coal cleaning plant. Classifying cyclones and spirals were found to play integral roles in the fractionation of minerals into the waste streams. The differences in the mineralogy, therefore, resulted in variation in leaching characteristics.

7- Long-term leaching characteristics of the coarse and fine refuse streams of three U.S. processing plants treating high, medium and low pyritic bituminous coal seams were examined. When placed in contact with water, the coarse refuse of the high and medium pyritic sulfur coals generated the most acidic conditions (pH~3) throughout the test period, while the pH of supernatant liquids in contact with fine refuse samples and coarse refuse of low pyritic coal were close to neutral. The elemental data analysis suggested that most of the trace elements were released under the acidic pH conditions in which pyrite oxidation was elevated by the ferrous iron ions in the leachate. Therefore, an effective strategy to minimize the release of trace elements is keep the medium pH close to neutral.

8- The highest amount of trace element release was obtained from dynamic leaching column tests involving the high and medium coarse refuse materials, while the least amount of released trace elements were related to low pyritic refuse streams. This suggest that higher pyrite content of the coarse refuse streams is the cause of acid generation and release of trace elements to the effluent. As a result, separation and isolation of the high density fraction, i.e. pyrite, of coarse refuse streams prior to the disposal minimize the environmental impact of coal waste disposal significantly. Subsequent co-disposing of remaining coarse refuse with fine refuse streams can buffer the supernatant water through the release of the self-buffering capability of the fine refuse stream. This also can suppress the oxidation of low remaining pyrite content in the system, due to any inefficiency of the separation processes.

9- In order to develop strategies to minimize the conductivity level of discharged water from coal refuse, long term leaching characteristics of refuse streams from processing plants treating low and high pyritic Appalachian coal seams were examined as a function of density. The results showed that removing material with S.G. greater than 2.68 from the coarse refuse of low pyritic coal, which represented 1.6% of the waste material, results in a reduction of the conductivity level to values below 500 µS/cm, which is the conductivity limit for Appalachian perennial streams.

10- For the high pyritic Appalachian coarse refuse sample, excluding 2.95 SG sink material which represented 4.4% of the total refuse material decreased the average electrical conductivity from 3834 µS/cm to 1250 µS/cm (62% reduction). Additional exclusion of 2.68 x 2.95 S.G. material which is only 0.5% of the total materials, resulted in further %6 reduction of EC and the leachate of the average of EC of remaining material (2.68 float fraction) was 1250 µS/cm. This significant reduction of EC of the leachate could significantly reduce downstream physical or chemical treatment of the leachate prior to discharge.

11- Comparison of the conductivity results from the separation of high density material from sub-streams of coarse refuse stream suggested that the conductivity of the leachate can be further decreased if material is crushed to a top size of 1mm. The particle size reduction created liberation of the minerals having natural buffering capabilities and of the high density fractions which made the separation process more effective.

12- The density separation required for separation and isolation of high density material in refuse streams can be easily achieved by modifying the coal processing plants for the treatment of the refuse material prior to disposal. This study suggested the addition of mineral spirals to the fine circuit for treating the spiral refuse stream, crushing the coarse and intermediate size fraction circuits (dense medium vessel and dense medium cyclone) to a top size of 6.35 and rejecting the high density fractions through density based separators.

6.2 Recommendations for Future Work

Based on the research work performed, the following recommendations are suggested for future work with excellent avenues for research improvements in this field:

1- The short term conductivity screening-level tests demonstrated relative liberation of high generating EC materials where the coarse refuse samples are crushed down to 6.35 mm. However, such fractions were more liberated where the coarse refuse material were crushed down to 1mm top size. Long term leaching evaluations in this study addressed the effectiveness of crushing coarse refuse samples to 6.35 mm top size for liberation and segregation of high density fractions for minimizing environmental impacts of coal waste disposal. For improving the hypothesis suggested in this research which separation and isolation of high density fractions, future work can conduct long term leaching evaluation study of segregation of high density material after the samples are crushed down to 1mm.

2- Application of multi-gravity separation (MGS) technology for rejecting high density fraction of fine refuse streams, followed by long term leaching characteristics of its product streams is suggested to be performed for further decrease of EC of supernatant liquid in contact with fine refuse streams.

3- Application and efficiency evaluation of different separation technologies to reject the high density fraction material in refuse streams Economic analysis of segregation of high density fractions after crushing the samples to 6.35 and 1mm needs to be performed.

4- Geotechnical analysis is suggested to be performed for stability analysis of making embankment of impoundments using coarse refuse materials with 6.35 and 1 mm top sizes.

5- The elemental analysis of density fractionated samples (See the Appendix) demonstrated that after the segregation of 5% high density material, the remaining %95 material contain close to 400 ppm of rare earth elements. Recovery of rare earth elements from coal processing refuse streams can provide significant avenue for coal mining company, and it could pay-off the further refuse stream treatments. Evaluation of rare earth elements extraction from coal refuse streams, therefore, would be extremely significant for achieving sustainable coal waste disposal from which valuables can be recovered for commercial use while the remaining materials are processed to generate environmentally benign material.

6- Acid mine drainage may result in release of significant amount of lithophilic and calcophilic trace elements. Evaluation of processes to recover the elements from acid mine drainage in coal mining could also provide significant improvement for sustainably coal waste disposal.

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VITA

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Peer-Reviewed Publications:

1. Ghosh, T., Rezaee, M., Honaker, R.Q., and Saito, K., 2014, "*Scale and Numerical Modeling of an Air Density-Based Separator*", In: Progress in Scale Modeling, Vol II, Ed. Saito, K., Ito, A., Nakamura, Y., and Kuwana, K., ISBN: 978-3-319-10308-2, Springer, pp. 225-239.
2. Rezaee, M., Huggins, F. E., and Honaker, R. Q., 2013, *"Minimizing the Environmental Impacts of Coal Waste Disposal"*, In: Environmental Considerations in Energy

Production, Ed. Craynon, J.R., ISBN: 978-0-87335-380-9, Society for Mining, Metallurgy, and Exploration (SME), pp. 60-76.

3. Zhang, W., Rezaee, M., Bhagavatula, A., Li, Y., Groppo, J., and Honaker, R.Q., 2015, "*A Review of the Occurrence and Promising Recovery Methods of Rare Earth Elements from Coal and Coal Byproducts*", International Journal of Coal Preparation and Utilization.
4. Rezaee, M., Huggins, F. E., Honaker, R. Q., and Hower, J. C., "*On the Removal of Hexavalent Chromium from a Class F Fly Ash*", Journal of Waste Management, Accepted.
5. Rezaee, M., Osanloo, M., Novak, T., and Honaker, R.Q., "*Open Pit Push Back Design: Criteria – Number and Characteristics*" International Journal of Mining and Mineral Engineering, Accepted.
6. Fazeli, M., Osanloo, M., Rezaee, M., and Honaker, R.Q., *"A Sustainable solution for Facilities' Location Selection in Open-Pit Mines"*, International Journal of Mining, Reclamation and Environment, Submitted.
7. Rezaee, M., Honaker, R.Q., and Warner, R., "*Development of a Field Leaching Test for Electrical Conductivity Screening-Level",* Science of the Total Environment, Submitted.
8. Rezaee, M., Honaker, R.Q., "*Leaching Characteristic Study of coal Processing Waste Streams",* The International Journal of Coal Geology, Submitted.

Conference Papers and Presentations:

1. Honaker, R.Q., Rezaee, M., Bhagavatula, V.A., Zhang, W., and Groppo, J., 2016, "*Potential Recovery of Rare Earth Minerals from Bituminous Coal*", SME Annual Meeting, Phoenix, AZ.
2. Luttrell, G., Kiser, M., Yoon, R.H., Bhagavatula, A., Rezaee, M., Honaker, R.Q., 2016, "*Characterization of Rare Earth Element Concentrations in the Product Streams of Coal Preparation Plants in the Eastern United States*", SME Annual Meeting, Phoenix, AZ.
3. Honaker, R.Q., Groppo, J., Bhagavatula, V.A., Rezaee, M., and Zhang, W., 2015, "*Recovery of Rare Earth Minerals and Elements from Coal and Coal byproducts*", AIChE Annual Meeting, Salt Lake City, UT.
4. Rezaee, M., and Honaker, R.Q., 2015, "*Evaluation of a Modified Leaching Test for Mining and Processing Byproducts*", Environmental Consideration in Energy Production Conference, Pittsburgh, PA.
5. Rezaee, M., and Honaker, R.Q., 2015, *"Sustainable Coal Waste Disposal"*, SME Annual Meeting, Denver, CO.
6. Fazeli, M., Osanloo, M., Rezaee, M., and Honaker, R.Q., 2014, *"Mine Facility Location Selection in Open-Pit Mines Using a New Multistep-Procedure"*, SME Annual Meeting, Salt Lake City, UT.
7. Rezaee, M., and Honaker, R.Q., 2014, *"Innovations in Coal Waste Disposal to Minimize Environmental Impacts"*, SME Annual Meeting, Salt Lake City, UT.
8. Ghosh, T., Rezaee, M., Honaker, R.Q., and Saito, K., 2013, *"Scale and Numerical Modeling of an Air Density-Based Separator"*, 7th International Symposium on Scale Modeling (ISSM-7), Hirosaki, Japan.

9. Rezaee, M., Huggins, F. E., and Honaker, R. Q., 2013, *“Minimizing the Environmental Impacts of Coal Waste disposal”*, Environmental Considerations in Energy Production Symposium, Charleston, WV.
10. Rezaee, M., Huggins, F. E., and Honaker, R. Q., 2013, *“Strategies to Minimize the Release of Trace Elements from Coal Waste Sources”*, SME Annual Meeting, Denver, CO.
11. Rezaee, M., Huggins, F. E., and Honaker, R. Q., 2012, *“Development of Strategies to Minimize the Release of Trace Elements from Coal-Waste Impoundments”*, Poster Presentation, SME Annual Meeting, Seattle, WA.
12. Rezaee, M., Osanloo, M., and Honaker, R.Q., 2011, *“Optimizing the Number of Open Pit Mine Push Backs”*, SME Annual Meeting, Seattle, WA.
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14. Rezaee, M., Karimi, M., Maarefvand, P., and Shahmoradi, J., 2009, *“Support System Design in Soft Rocks”*, 8th Iranian Tunneling Conference, Tehran, Iran.
15. Rezaee, M., and Osanloo, M., 2009, *“The Optimum Number of Open Pit Mine Push Backs”*, 18th International Symposium on Mine Planning & Equipment Selection (MPES), Banff, Alberta, Canada.