

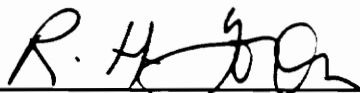
**CHEMICAL and ELECTROCHEMICAL COAL CLEANING in ACIDIC MEDIUM
APPLICATION and ANALYSIS of the PROCESS**

by

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Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
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in
Mining and Minerals Engineering

APPROVED:



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(ABSTRACT)

The Chemical and Electrochemical Coal Cleaning (CECC) process, designed to remove mineral matter from coal, has been investigated by treating coal samples in acidified slurries. Various coals, characterized by different maceral structures and mineral matter contents, were subjected to several experimental procedures under mild conditions.

Substantial amounts of mineral matter (up to 70%) could be extracted from coals which were resistant to physical cleaning, while 22% of sulfur could be removed from pyritic coals. The operating conditions of the CECC were studied in order to determine their influence on the process efficiency.

Analyses conducted on solids and leachates resulting from the tests demonstrated that different mechanisms were achieving demineralization by the CECC. Between 50% and 95% of the feed mineral matter was removed by dissolution, whereas the balance could be ascribed to liberation. The CECC process is suitable for cleaning middlings, as well as for further extracting mineral matter from physically clean coals, especially from pyritic vitrinite and fusinite type coals.

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1.0 INTRODUCTION

1.1 Preamble

Low-ash coal is needed for many applications in energy supply or industrial use, when it may be substituted for petroleum products. One of the applications of low-ash coal is to provide power. During combustion, the mineral matter contained in coal macerals may be released as airborne particles and hazardous gases (above all sulfur dioxide) which are harmful to the environment. The uncombustible mineral matter turns into ash that forms slags on turbine blades and damages the equipment. It is therefore necessary to remove as much mineral matter as possible from coal prior to its combustion.

Physical coal cleaning methods are commonly used to remove mineral matter from coal. Heavy-medium separation is widely used for cleaning coarse coal (above 500 μ m), while froth flotation is used to clean fine coal smaller than 300 μ m. Fines and ultrafines may be cleaned by flocculation, coagulation or microbubble flotation.

However, some coals, particularly low rank coals, are unresponsive to these physical methods, so that research on alternative processes is needed. In addition, grinding is the more expensive step of the physical cleaning of coal; therefore, research in new methods involving coarse particles is needed.

The new methods should meet the following requirements: an economic process that can achieve high recovery of a low-ash product. The new method may consist of one or more than one processing step, each step being designed for a specific purpose. The new process could be an additional step to a conventional coal cleaning process. For example, a coal that has been cleaned by a physical method may be chemically treated to further reduce its ash and sulfur contents. Depending on the coal, the new method may as well be used to process the whole combustible.

CECC may be one of these alternative processes. Nowadays, research on coal desulfurization by chemical leaching is being intensified, because of the inefficiencies in physical coal cleaning processes. Only a few investigations have been made in acidic media, while more attention has been paid to the mineral matter extraction in basic media. Furthermore, extracting the mineral matter which is the minor constituent of coal with aqueous solutions should be more economical than the liquefaction process which dissolves the whole organic matter with expensive organic solvents.

Chemistry-based extraction of mineral matter should not be aimed at removing free minerals, because it may result in an excessive consumption of reagent. Furthermore, free minerals can be easily removed using conventional physical techniques. Therefore, CECC should be aimed at separating and removing minerals tightly bound to or trapped inside the coal matrix, which can not be removed by physical techniques unless a long and expensive grinding step is employed.

Chemistry-based processes exist to extract mineral matter; alkaline treatments are efficient, especially on quartz and kaolinite (Waugh and Bowling, 1984). However, the

high temperature and pressure involved induce high investment and operating costs. On the other hand, the acid-based CECC, despite a lower efficiency, may be conducted within slurries at low temperature and at atmospheric pressure, and yield good ash reductions. The procedure applied for the CECC being fairly simple, the equipment required being easily supplied, and the reagents utilized being safe and widely used, the treatment of ground coal in acid solutions appeared to be an attractive process to be developed.

CECC carried out in an acid medium allows different mechanisms to take place. In addition to mineral matter dissolution due to the solution acidity, other phenomena are expected to improve liberation and dissolution of mineral matter. The treatment of coal in acidified slurries, intensely studied in the past decade, was demonstrated to oxidize readily the coal surface (Farooque and Coughlin, 1979, Okada et al., 1981, Dhooge et al., 1982). Furthermore, strong oxidation of the coal is believed to favor a phenomenon of osmotic pressure, taking place inside the maceral cracks, and at the interface between minerals, or between coal and minerals (Yoon and Paul, 1987), and liberating mineral matter. A model was developed (Paul, 1988), which predicts the oxidation of the surfaces, the consequent attraction of ionic species into the interstices, and the resulting flux of water towards the inside, which creates an osmotic pressure that may be sufficient to open the coal cracks, or separate mineral matter particles from the coal. Ferric ions are known to act as a catalytic agent liable to oxidize the coal surface; since a very low pH is required to reoxidize ferrous ions into ferric as well as to keep ferric ions at their highest oxidation level, an acidic medium was necessary to carry out the CECC.

1.2 Description of the CECC Process

The procedure applied was fairly simple. A typical experiment involved the following steps:

- The feed coal, ground, sieved and pre-washed at the required size, is mixed in a vessel with an acid solution at the right temperature.
- The slurry thus formed is stirred during a given period of time at a constant temperature; electrolysis can be applied in order to increase the solution potential in the anodic compartment of the vessel; this case is called "electroleaching" (EL). Chemicals such as ferric ions can be added into the slurry to enhance the oxidation level of the slurry. "Simple leaching" (SL) will refer to the case where no electrolysis is applied. The mechanisms mentioned above take place from the beginning of the procedure until reactions are completed. A few hours are usually necessary, but some coals may require longer processing times.
- After processing, the slurry is rinsed with tap water onto a screen to separate the solid product from the solution and from the fines produced during the treatment. Each sample is then dried for analysis.
- Analyses on feed coal, on product coal and on tailings, as well as on leachate, are used to quantify the amount of mineral matter extracted from the feed coal and to characterize the mechanisms by which this mineral matter could have been extracted.

1.3 Working Principles

The mineral matter is extracted basically by two means: by chemical dissolution and by liberation. Liberation and dissolution of mineral matter depend on coal type, percent solid, particle size, processing time, temperature, acid type and concentration, oxidation level, and stirring speed.

Moreover, a high oxidation level and the presence of ferric ions in the slurry were reported to improve the oxidation of the surface of coal, and therefore favor the build-up of electrical double-layers with ions attracted from the electrolyte (Paul, 1988). The osmotic pressure should then be enhanced, and consequently favor the liberation of the particles.

1.4 Purpose of this Study

The first objective of the present study was to apply extensively the CECC process described above to evaluate its potential to clean different coals. This included a series of preliminary tests designed to find out the best responding coals and the ideal operating conditions by determining how much of their mineral matter was removed.

The second objective of this study was to conduct convenient analyses on the most propitious coals, and to elucidate the different mechanisms involved in the CECC. This was necessary to evaluate the mineral matter present in the coal feed and product, and to determine how much was removed by liberation and by dissolution. This also re-

quired visual examination of the particles of feed and product samples to attempt to comprehend the process.

1.5 Chapter Outline

Chapter 2 gives the literature review on coal structure and various processes for chemically removing mineral matter from coal.

Chapter 3 presents the materials and the equipment used to carry out the experiments, as well as the details of the procedures adopted in the various experiments.

Chapter 4 details the extensive series of experiments conducted in order to meet the objectives defined in the introduction. The first section deals with the experiments designed for cleaning the various coals, while the second section focuses on the systematic study of a selected coal (Wyodak coal), to determine the optimum operating conditions.

In chapter 5, the first section deals with analyses carried out on selected coal samples (Wyodak and Widow Kennedy). These analyses involved x-ray to determine the minerals present, mass balance calculation to quantify dissolution and liberation, and electron microscopy to determine the way minerals were removed. The second section proposes an interpretation of the previous analyses intended to provide a better comprehension of the whole process.

Chapter 6 summarizes the main conclusions about the application of the process and the main mechanisms involved. The chapter ends with guidelines proposed for future work on the topic.

2.0 REVIEW of LITERATURE

2.1 COAL STRUCTURE

Coal is a heterogeneous composite material basically made of an organic carbon matrix (60-95%) and inclusions of various types of minerals. Biochemical (bacterial) degradation of plant debris such as cellulose, lignin, resins and waxes, is responsible for maceral formation. Further metamorphosis under high temperature and pressure over long periods leads to the usual coal structure. The more advanced the metamorphosis, the higher the coal rank (percent fixed carbon). The mineral matter is included in coal either by drainage and entrapment of fine particles in the forming macerals, or by chemical reaction involving aqueous solutions during the metamorphosis.

Like Figure 1 shows (Wiser, 1987), the molecular structure of most coals consists of arrangements of aromatic carbon rings (ϕ) fused together into small clusters, themselves linked by different bondings: ϕ - ϕ , ϕ -O- ϕ (ether) or open chain C-C (aliphatic). Usually, phenolic (ϕ -OH), hydroxyl, quinone ($\phi = O$) and methyl (ϕ -CH₃) groups are

attached to the carbon rings. Organic sulfur is present when attached to the aromatic structures (such as thiophenes).

2.1.1 Coal Classification

The ASTM definition for the coal rank states that the rank of a coal is defined by “its degree of metamorphism, or progressive alteration, in the natural series from lignite to anthracite ” (ASTM, 1979). The usual classification by increasing rank is the following:

- Lignite
- Sub-Bituminous
- Bituminous
 - Low-rank*
 - Medium-rank*
 - High-rank*
- Anthracite
 - Semi-anthracite*
 - Anthracite*
 - Meta-anthracite*

As for high-rank coals, the higher the fixed carbon value, the higher the rank of the coal. For low-rank coals, the higher the calorific value, the higher the rank. In general, a higher rank coal will not only contain less linear polymers, less hydrocarbons, less CO₂, less oxygen groups and less moisture, but also improved carbon aromaticity and reflectivity to incident light. The cleat network is also known to improve with the coal rank until low-volatile bituminous stage is reached; at higher ranks, the fracture system will be less developed (Ting, 1982).

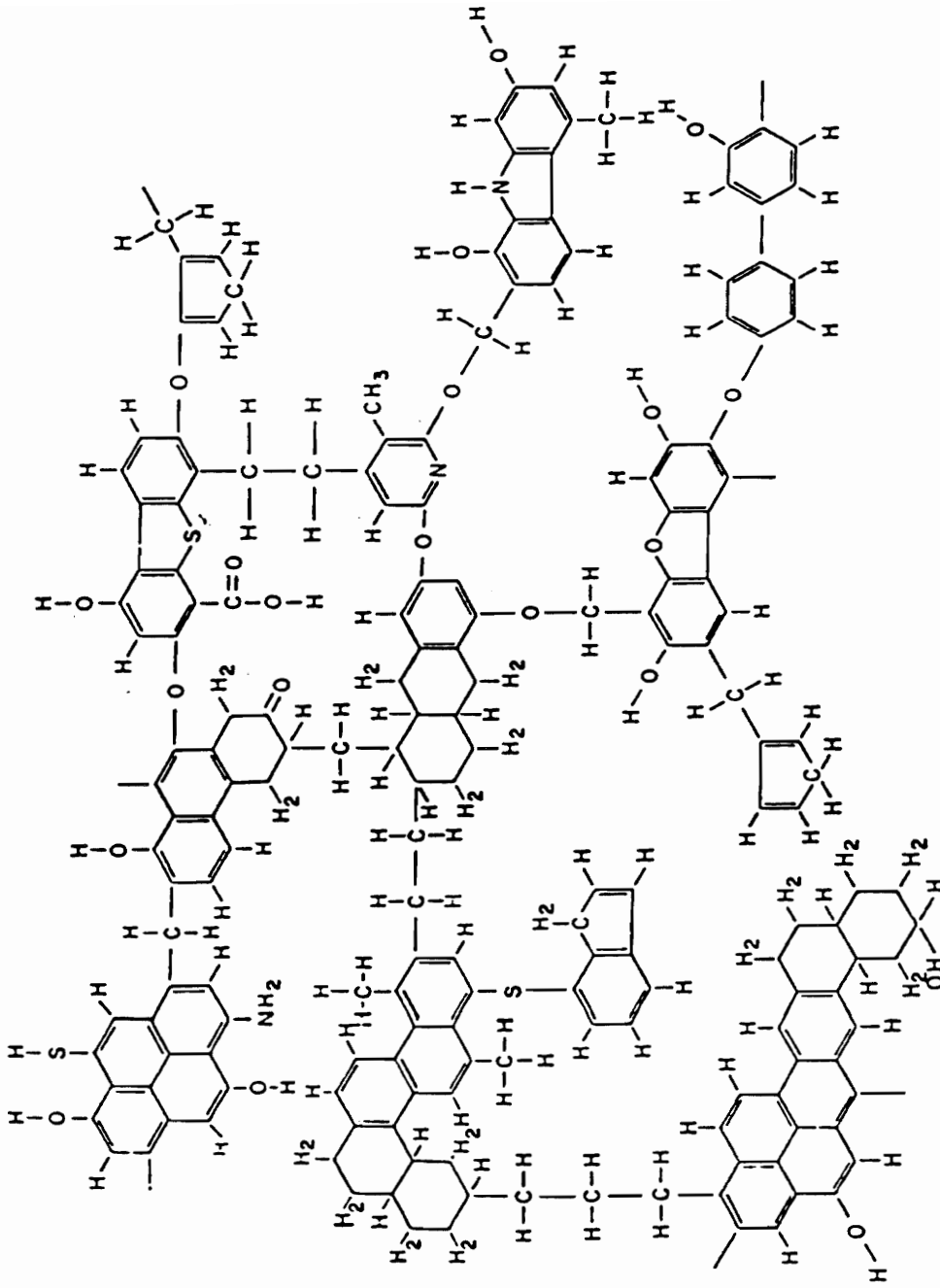


Figure 1. Structural groups and connecting bridges in bituminous coal (Wiser, 1987)

2.1.2 Macerals in Coal.

Three major types of macerals composing the organic matrix of most coals (Ting, 1982) can be distinguished.

2.1.2.1 *Vitrinite*

Originating from the decomposition of woody stems, roots, bark and leaves, this type of maceral is the most abundant one (70-80%). Its lightly anisotropic matrix is fairly compact, and appears to be band or lens shaped. The cleat (fracture system) is well developed, microscopically as well as macroscopically and the grinding resistance is known to be low. Vitrinite is characterized by a medium density and a high moisture content. It contains very few disseminated minerals, except pyrite. This maceral is easy to convert into liquid or gaseous fuel. Moreover, it is sensitive to post mining storage oxidation.

2.1.2.2 *Inertinite*

Inertinite comes from woody tissues that were charred during swamp fires. It is therefore very stable and chemically inert, so that little macerals transformation occurs during metamorphosis. Some hydrogen can remain when not all tissues have been burned; when this is the case, these materials should degrade into vitrinite-type macerals. Inertinite represents about 10 to 20% of the coal macerals, and exists mainly as fusinite. Its structure is clearly fibrous but the material is amorphous and isotropic. In general, inertinite contains more aromatized carbons and less hydrogens than any other maceral,

while its density is the highest. Most of the time, the pores are filled with clay-type minerals.

2.1.2.3 Liptinite

Liptinite (exinite) is issued from resins and waxes and is available in small amounts (0-7% of the organic matter) which is composed of very small grains (minus 100 μ m). Extremely porous, this substance has the lowest density among macerals, and because of its plate-like structure, it is the most anisotropic. Liptinite contains little moisture but much hydrogen, and is readily converted into liquid or gaseous fuels.

2.1.3 Mineral Matter in Coal

The above mentioned coal macerals usually contain a considerable amount of mineral matter, that is various crystalline forms. The average size of mineral particle is 20 μ m, thus much smaller than any maceral body. The genesis of these minerals follows various patterns (Renton, 1982). The mineral matter may appear at the beginning of coalification (syngensis), or after the coal has already been formed (epigenesis).

Some "vegetal" mineral matter is already contained in plant fibers (especially in leaves and bark) before they die, while detrital mineral matter may be inserted in the seam as it forms, generally as quartz and clays brought by erosion. However, some mineral matter forms in the coal matrix by precipitation of dissolved ions from aqueous solutions. These solutions transported dissolved mineral matter from the swamp environment, and then reacted with some organic (or inorganic) elements released by

macerals during decomposition. The Pocahontas Basin coals, for example, contain approximately 40% kaolinite, 16% illite and 30% quartz, 3.5% pyrite, 2.5% calcite, 1% dolomite and 1% siderite.

2.1.3.1 *Typical Mineral Matter in Coal*

Kaolinite $[Al_4Si_4O_{10}(OH)_8]$ is one of the most common syngenetic mineral matter, and is found in between the coal planes, dispersed throughout vitrinite, or filling fusinite cells, and other macrofractures in coal. However, kaolinite is also the only clay found in epigenetic formation.

Illite $[KAl_2(AlSi_3O_{10})(OH)_2]$ is always mixed with kaolinite and located mainly in bedding planes. Illite is found neither disseminated through the coal matrix, nor filling pores or cracks; it should therefore be absent from physically cleaned coal.

Other mixed-layered clays are quantitatively hard to evaluate, and are more abundant in low-rank coal seams. Water penetrates easily the layer structure of clays, and can swell some of them (such as montmorillonite). Clays also show cation exchange characteristics with many inorganic (and organic) ions in solution (Leja, 1982).

Quartz $[SiO_2]$ is typically syngenetic, from detrital, vegetal or chemical origin (Renton, 1982). Some vegetal amorphous silica may also have dissolved and recrystallized into SiO_2 . Quartz is present as tiny particles, from micron-size grains to very small crystallites.

Carbonates are usually ranked third among mineral matter components in U.S. coals. They are usually formed during late stages of syngensis.

Calcite $[CaCO_3]$ is the most common carbonate, often filling up cavities and cleats. Calcite is often associated with *dolomite* $[(Ca,Mg)CO_3]$.

Siderite [FeCO₃] whose metamorphism involves non-marine or non-alkaline waters, and low reducible-sulfate ions (like in the Southern Appalachian Basin or the Western States) and is often combined with calcite.

Pyrite [FeS₂], is the most abundant sulfide in coal (Brown et al., 1952). Pyrite is mostly found in vitrinite (or in inertinite as a cementing agent), as framboids, euhedral crystals, irregular shaped crystals or as fracture filling materials (Renton, 1982).

- *Framboids* are made of a group of tiny crystals (0.1 to 2µm), forming typical spheres of 10 to 200µm in diameter. The crystals are most often cemented together by fine pyrite powder, and in rare cases, by kaolinite (Scheihing et al., 1978). Framboids are abundant in vitrinite matrix, in bedding planes or in cavities.
- *Euhedral Crystals* look like the crystals composing framboids, except that they are not assembled together.
- *Irregular-Shape* crystals are most often inclusions in fusinite pores or substitutions of maceral groups in vitrinite bodies (high sulfur coals).

Sulfates in coal include calcium complexes such as bassanite [CaSO₄-1/2H₂O], anhydrite [CaSO₄], and gypsum [CaSO₄-2H₂O]. Some iron sulfate [FeSO₄] is not rare.

2.1.3.2 *Combinations of Minerals in Coal*

Depending on the chemical nature of the coal fields, some associations of minerals can occur. At low pH, the low bacterial activity preserves the organic matter in vitrinite, and most ions remain in solution; in this case, kaolinite formation is enhanced. On the

contrary, at higher pH, most ions precipitate and favor illite formation. Therefore, the ratio of kaolinite over illite in coal formation depends on the pH of the ground.

It is often observed that pyrite and calcite contents vary the same way. Furthermore, with low pH solutions containing limited amount of sulfates, siderite is favored against pyrite, whereas with higher pH solutions containing more sulfates, pyrite is favored

2.2 OSMOTIC PRESSURE

2.2.1 Osmotic Pressure Inducing Mineral Matter Liberation

A general mechanism, termed "Electrocatalytically Induced Liberation" of mineral matter (EIL), studied and reported by Paul, (1984 and 1988), and a patent obtained by Yoon and Paul (1987), describe an electrochemical process designed to liberate mineral matter from coal. The mechanism of this method is believed to occur from the build-up of an osmotic pressure in coal crevices inducing the liberation of the trapped mineral particles.

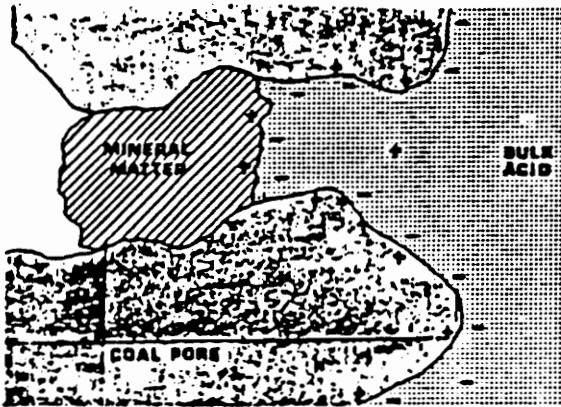
The surface of a coal submitted to an acidic electrolyte containing oxidizing ions is becoming oxidized. This is the result of an oxidation initiated by the reduction of ferric ions to ferrous ions on the surface and on the crevice walls inside the macerals. The oxidation of the surface by the ferric ions involves the breakage of sessile bonds from the matrix and the transfer of electrons to the ferric ions which are reduced to ferrous ions. This oxidation is believed to destroy part of the cross-linked coal structure and open up

the cracks. The spent ferrous ions can be electrochemically regenerated to ferric ions at the anode placed in the coal slurry, this anode delivering a potential higher than the equilibrium potential of the ferrous-ferric couple.

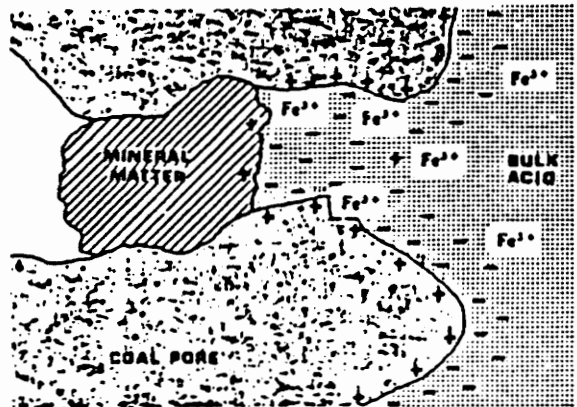
Most of the minerals in coal being positively charged in strong acid solution, the charging process of the solids should create repulsion and, if the pore is large enough, dislodge the minerals. If the pore is narrow, the mineral surface charging should contribute building-up a greater positive charge inside the pore. This should enhance the migration of the electrolyte negatively-charged ions towards the inside of the pores and result in the build-up of electrical double-layers, under favorable electrolyte and pore size conditions. The high ionic concentration resulting from the overlapping of these double-layers should play the role of a semi-permeable membrane, and induce a Donnan potential gradient (unequal distribution of ions across a membrane or a charged surface). This gradient induces an imbalance in the chemical potential of water, reduced inside the pore and maximum outside in solution. As a consequence of this imbalance, the water is forced to flow inwards through the "ionic membrane", which builds up an osmotic pressure, which may be high enough to open the crevice. If this is the case, the electrolyte flows inside and leaches mineral matter; in case of wider openings, the mineral matter entrapped in the matrix shall be liberated. This principle is illustrated by Figure 2. The fine liberated particles can then be removed from the product coal by an appropriate means, such as screening or microbubble flotation.

A thermodynamic model was developed (Paul, 1988), based on Donnan equilibrium and depending on parameters such as pore size or electrolyte type. Pressures of 4 to 7 atm should build up in fissures 100 to 1000Å in width, as shown in Figure 3.

Many coals were processed, and the significant ash reductions were ascribed to the EIL process. The improvement noticed for the EIL process over simple acid leaching



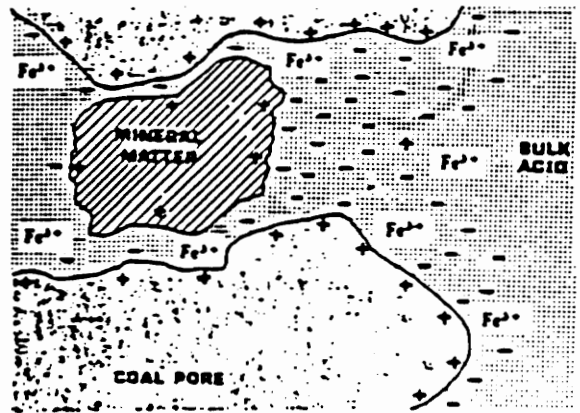
Step I: The coal surface acquires a positive surface charge in the acidic medium ($\text{pH} \leq 1.0$). A double layer of counter-ions forms along the coal surface.



Step II: The reaction of ferric ions with the coal increases the charge on the coal and attracts more counter-ions to the vicinity of the coal surface.



Step III. The increased ion concentration inside the pore reduces the aqueous chemical potential. The hydrostatic pressure inside the pore increases to equalize the aqueous chemical potentials inside and outside the pore.



Step IV: The increased hydrostatic pressure fractures the pore and loosens the mineral particle. This in turn allows the electrolyte to penetrate further into the pore. Steps I-IV may be repeated to liberate other mineral particles embedded deep inside the pore.

Figure 2. Stages in the Liberation of a Mineral Particle Inside a Coal Pore During EIL Process (Paul, 1988)

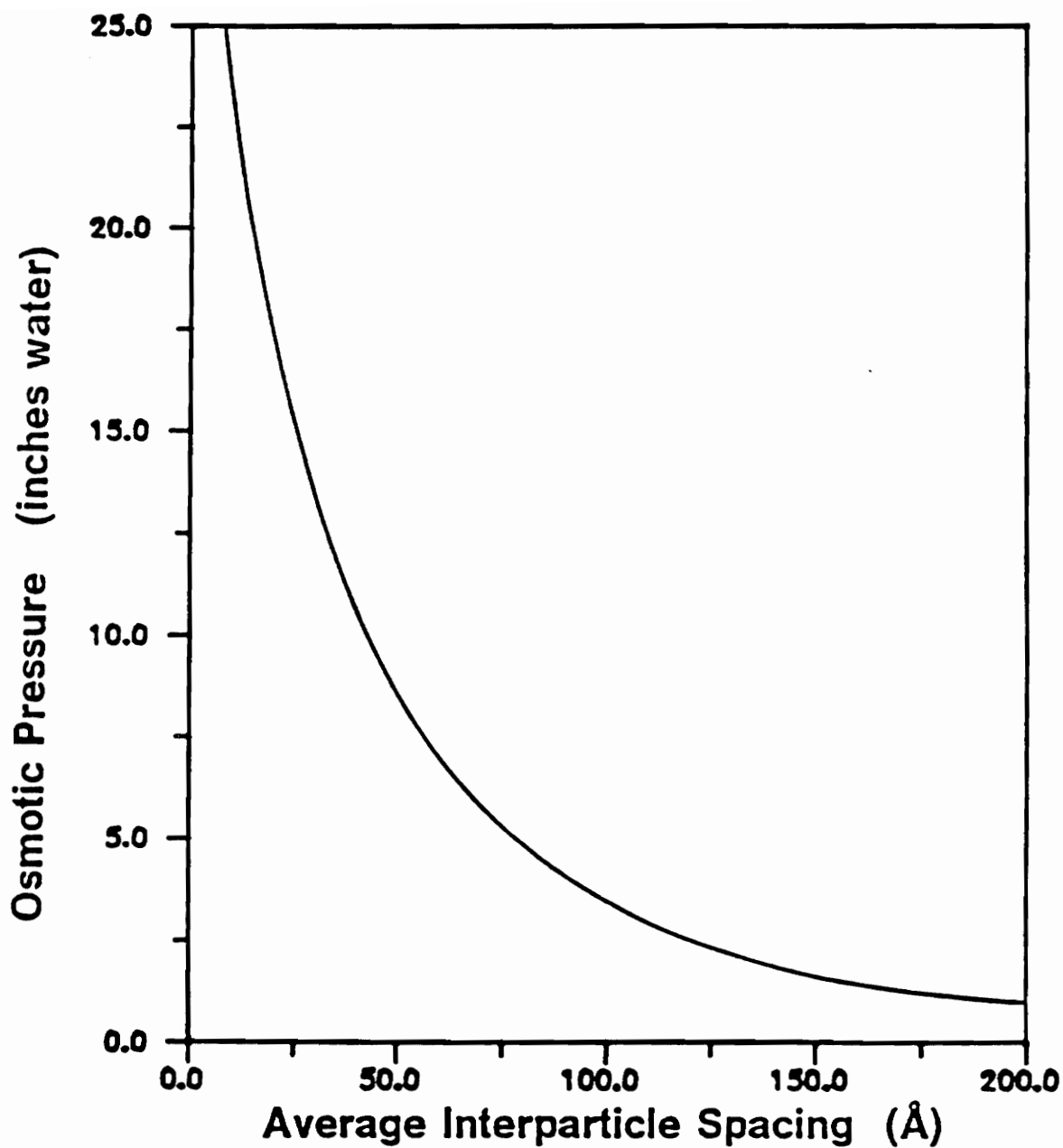


Figure 3. Theoretical Osmotic Pressure Developed Inside a Fine Quartz Bed in Sulfuric Acid (Paul, 1988)

was said to be due to the increase in the coal surface oxidation, itself due to the action of positive charges (such as ferric ions).

2.2.2 Osmotic Swelling of Clays

Clay-water systems were intensely studied in mineral processing, as well as in geology and in foundation engineering. Clays are made of compact aggregates of very fine plates, liable to attract water molecules from the surroundings and induce hydration phenomena. Three major forces govern the adsorption of water between clay layers: Van der Waals attraction, electrostatic repulsion and hydration interactions. Clay layers are likely to be pushed apart from each other and swell according to two mechanisms: hydration swelling and osmotic swelling (van Olphen 1977).

Swelling due to Hydration results from the hydration interaction, that is the adsorption of monolayers of water molecules on the plates surface. The spacing between plates at which this hydration occurs is generally a few nanometers. Adsorption is energy based, and is characteristic of the layer adsorbed. The energy necessary to desorb the first monolayer of water from clays is usually very high. Analyses conducted with IR Absorption prove that hydrogen bonds, linking water hydrogens with silicate oxygens, are highly predominant.

Swelling due to Osmotic Pressure becomes predominant after four monolayers of water, reaching a spacing of about 10\AA , are adsorbed between the plates; at this point, the surface hydration energy is no longer important, and the governing force is based on electrostatic repulsion. Flakes of montmorillonite can swell until plate interspacing reaches 120\AA , while osmotic pressures develop up to several atmospheres. Osmotic swelling is limited by an increase of salt in the electrolyte, proving that the phenomenon

is based on double-layer repulsion. The gradient of ions concentration between inside the clay and outside in the electrolyte forces the water to drive towards the plates surface; an increase in ionic strength in the solution would then lower the attraction of water and consequently the swelling.

Swelling is limited however, and clays do not fall apart; at equilibrium distance between the plates, attracting Van der Waals forces should compensate the repulsion forces; however, these attraction forces are theoretically too weak, and another attractive force to be considered is a cross-linking force established by positive edge-negative face combinations of nonparallel plates. These cross-linking forces not only hold the clay structure together, but also reinforce the clay against compression by increasing its rigidity.

2.3 CHEMICAL TREATMENT of COAL

2.3.1 Mineral Matter Removal

In order to enhance combustion, coal can be separated from its mineral matter by a chemical process; most treatments usually require high pressure and temperature, and none offers commercial promise yet. Most time, a hot alkaline solution is used to convert quartz and clays into acid soluble products (Waugh and Bowling, 1984). Acid leaching then takes place followed by many stages of washing. The extraction of ash-forming minerals in bituminous coals was carried out using aqueous sodium hydroxide at 200-300°C under pressure (Waugh and Bowling, 1984). Most extracted species were

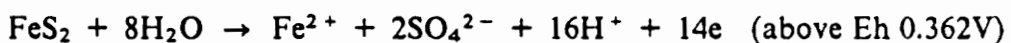
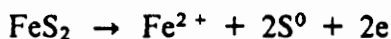
silica and kaolin that formed sodium aluminosilicates, not soluble in alkali, but readily soluble in acid; finally, spent leachates were recycled. High-sulfur coals were treated by NaOH-KOH at 320-400°C for 1 to 3 hours, then washed with acid (Norton et al., 1988); 60 to 90% of the ash was removed along with 25 to 90% of the sulfur, depending on temperature and reaction time.

Hydrothermal treatment of some coals in hot water - 300°C- was found lowering the ash and sulfur contents (Hippo et al., 1988). At higher temperatures, the organic matter devolatilizes. Some iron was found in the leachates and pyrite grains were missing on the coal surface.

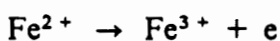
2.3.2 Sulfur Removal

2.3.2.1 Pyrite Oxidation

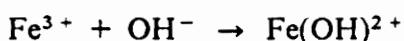
Below pH 2 and above Eh 0.421V, pyrite oxidizes and yields ferrous ions according to the following oxidation reactions (Biernat & Robins, 1972):



Below pH 1.1 and above Eh 0.771V, ferrous ions will be oxidized to ferric ions:

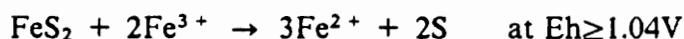


According to the Pourbaix Diagram from Garrels & Christ for the iron system, if pH > 1.1, ferric ions will undergo:



It is then necessary to maintain a very low pH to keep the ferric ions dissolved, as shown on the diagram for iron sulphides and oxides, from Harper and Row (1965), in Figure 4.

The reaction of pyrite oxidation may be autocatalytic (Lalvani & Shami, 1986):



since ferrous ions issued from pyrite are regenerated to ferric ions, which can oxidize pyrite.

2.3.2.2 Mineral and Organic Sulfur Removal

Over 60% of the total sulfur of a coal slurry can be removed by electrolysis in an alkaline media (Wapner et al., 1988). Mineral sulfur (sulfates and pyritic sulfur) decreased by 85% after 1 hour of electrolysis in NaOH 1M in the anodic compartment of the cell, at the potential 1.3V SCE. The higher the temperature, the higher the oxidation rate and the higher the anodic current. Like mineral sulfur, organic sulfur was efficiently extracted (at 70%) from the coal matrix, using electrolysis at high cell potential in NaOH, the temperature ranging from 27 to 80°C (Wapner et al, 1988).

The high selectivity of the H₂O₂-H₂SO₄ mix was discovered for sulfur oxidation (Vasilakos & Clinton, 1984). Pyritic sulfur oxidized to soluble iron sulfates (resulting in sulfur reduction from 1.3% to 0.2%). After prolonged exposure, organic sulfur was also oxidized. The mix had a synergic effect, and the optimum acidity was found to be around 0.1M of sulfuric acid. It should be noted that control of oxidation in any desulfurization process is important, since the heating value of the coal would be reduced if the coal is oxidized severely.

Yurovskii designed a method of cleaning coal based on acid leaching and desulfurization (1960). This process involved ferric sulfate solutions (oxidizing pyrite

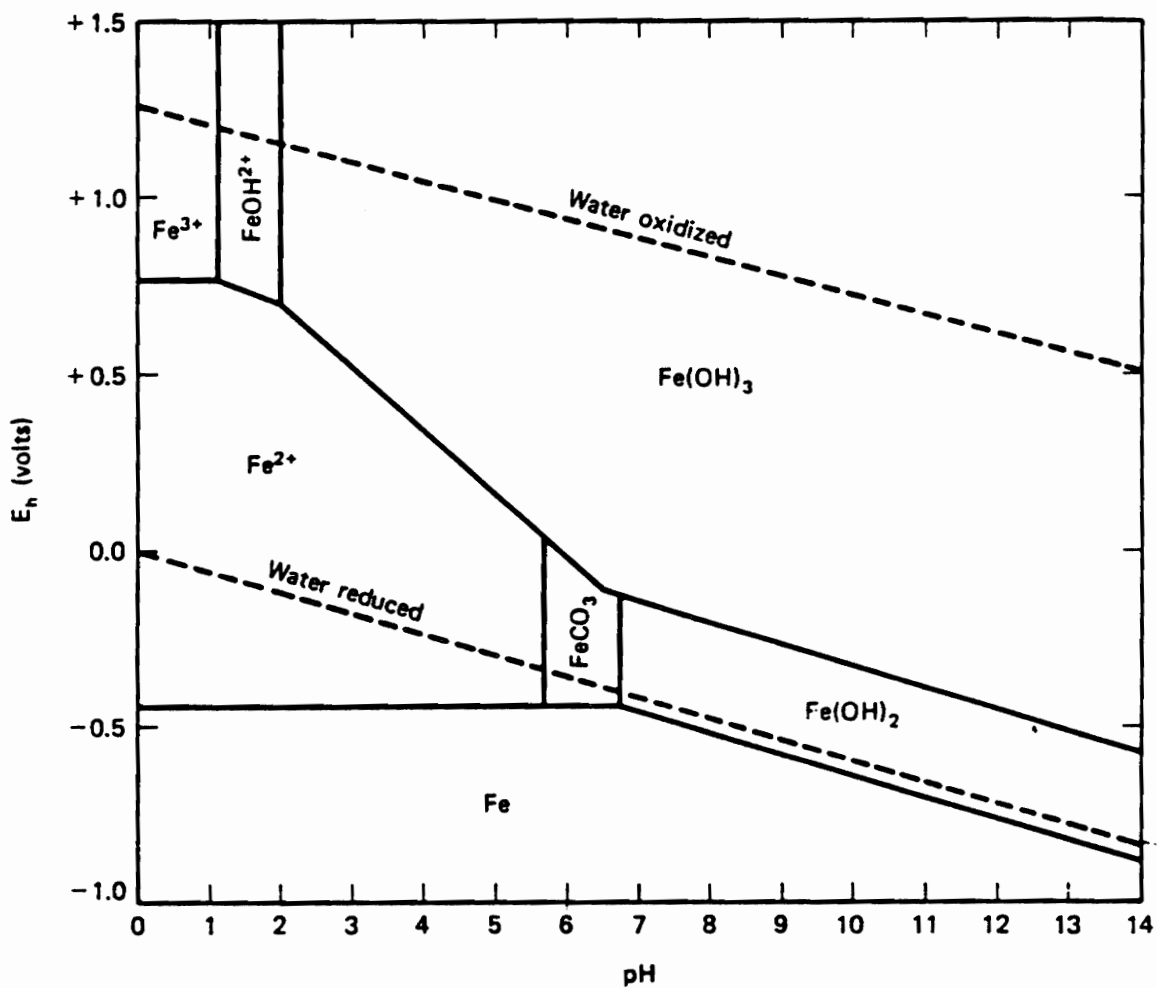


Figure 4. Eh-pH Diagram for Iron System (Harper and Row, 1965)

and elemental sulfur to sulfates) also containing nitric acid, both known as effective leachants of pyrite. This mixture was found to have a synergetic effect on pyrite extraction. Then, the coking properties of the coal were not affected as they would be with nitric acid alone. All the ferric sulfate required was provided by the process itself, pyrite being decomposed under the action of nitric acid into ferric sulfate. Finally, no elemental sulfur was left contaminating the coal as would have been the case with ferric sulfate alone. From a 25.8% ash and 5.82% sulfur coal processed in a pilot plant, a product assaying 4.5% ash and 2.17% sulfur was recovered.

Various other ways of cleaning coal of sulfur are reported (Meyers, 1977; Yoginder and Candle, 1988), and many others are presently being intensely investigated, since the protection of the environment from sulfur dioxide has become a real challenge.

2.3.2.3 Cracking of Coal

The reaction of a coal with anhydrous ferric chloride (dry process) in a ratio 3:1 by weight at 230°C during 1 hour under a nitrogen gas stream had significant effect. A tremendous network of cracks had developed and made the surface area of the coal increase by 35 times. Some FeCl₃ substances had recrystallized between the carbon planes, especially with high-rank coals (Beall et al., 1983).

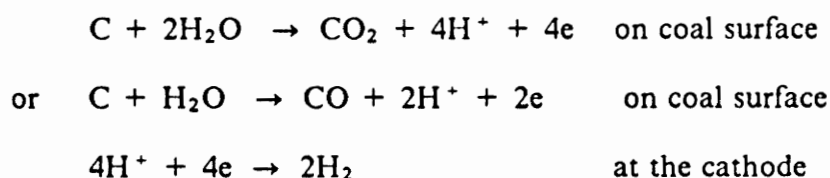
Chemical comminution of coal to generate slurries *in situ* can be achieved by a chemical process patented by Aldrich (1984). A reactive agent, pumped down to the seam, disjoins the coal grains and draws the slurry out. The disjoining mechanism is understood as a diffusion of the reagent into the reactive sites of the matrix, followed by ionic exchanges on polar bonds. The matrix swells and breaks, releasing coal particles into the liquid. The molecular size of the reagent and temperature are the most influential factors governing the process.

2.4 *ELECTROCHEMICAL TREATMENT of COAL*

2.4.1 Electrochemical Oxidation of Coal

Electrochemical oxidation studies were carried out to oxidize coal slurries. It was believed that coal gasification products (like CO and H₂), conventionally extracted by high temperature processes, could be obtained by a low temperature electrochemical treatment.

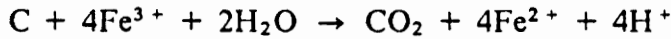
The anodic oxidation of a coal slurry in acid media using platinum or graphite electrodes (Farooque & Coughlin, 1979) was described as:



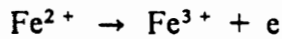
The carbon dioxide and carbon monoxide were produced in the anodic compartment, whereas the hydronium ions migrated through the glass frit wall toward the cathode, and collected the electrons necessary to form hydrogen. Coal is thought to be a good electron donor, hence a substance liable for oxidation. Along with anodic oxidation, oxides were formed on the surface (mostly carboxylic groups RCOOH). Sulfuric acid was readily regenerated, and was not consumed by the electrochemical gasification. The reactivity was improved by a decrease in particle size.

The idea of studying the current densities at the anode and the production of hydrogen at the cathode was developed by Okada et al. (1981) and Dhooge et al. (1982). By adding ferric ions, the oxidation was improved. Dissolved iron is more electroactive

than coal, and therefore is a good reaction catalyst. The reaction on the surface was as follows:

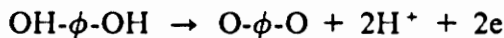


in which ferric ions are shown to be reduced to ferrous ions. The latter is then reoxidized to ferric at the anode by the following reaction:



Ferric ions can therefore be reused for the reaction, while the electrons supplied produce an anodic current. These two reactions are represented on Figure 5.

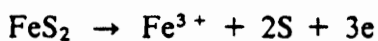
Other studies indicated that the primary step of electrochemical coal oxidation, in the potential range where $\text{Fe}^{2+}/\text{Fe}^{3+}$ reactions occur, involved mainly hydroquinone rings that were oxidized by ferric ions to quinone groups (Kreysa and Kochanek, 1985):



Very little CO_2 was formed, which was contrary to what Farooque and Coughlin found (1979). The above reaction was limited by the redox potential of the system.

2.4.2 Electrochemical Oxidation of Sulfur

The electrolytic oxidation of pyrite in acidic medium was described by Biegler and Swift (1981):



Pyrite removal is, therefore, possible by oxidation, producing sulfates and/or elemental sulfur as products. Thus, coal oxidation can occur either by directly contacting the anode and giving off electrons, or by transport of the ferric ions to the coal surface.

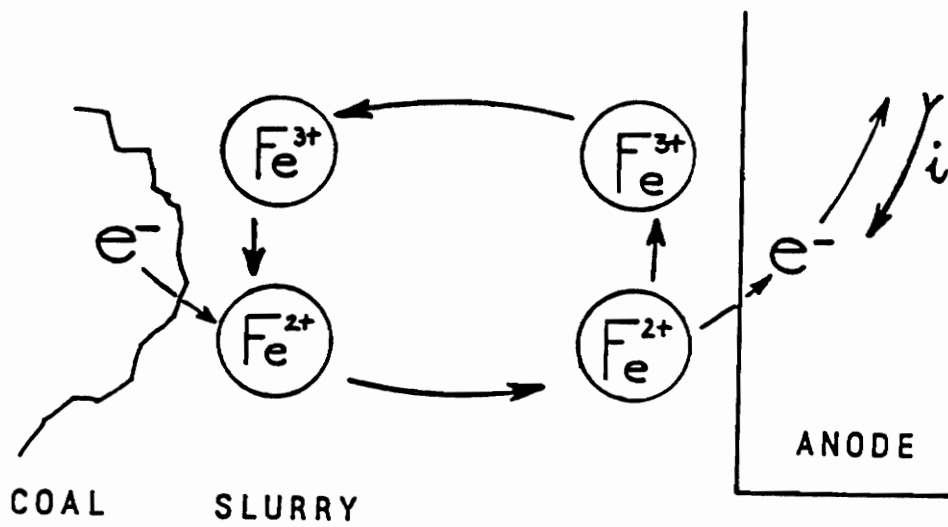


Figure 5. Representation of Coal Oxidation Via the Fe(II)/Fe(III) Redox Couple

Ferric ions are considered to migrate towards pyrite crystals or thiophene groups in macerals (Lalvani et al., 1983), and oxidize them into sulfates. At 60°C, 40% of the total sulfur was removed and the CO₂ emission was very poor. Pyrite, known to be insoluble at room temperature in dilute sulfuric acid, was found soluble in highly oxidizing conditions (i.e., at IV NHE) in concentrate acid at temperatures not exceeding 100°C; complete dissolution was achieved after 4 hours of processing.

Mild pyrolysis (50 to 350°C) of coal in alkali resulted in 70% of sulfur removal (Lalvani and Hines, 1988). This was due to breakage of scissile bonds (like aliphatic and ether), which induced depolymerization and created more access to sulfur. Ash removal and devolatilization of organic matter increased with the applied potential (up to 50% ash reduction).

3.0 EXPERIMENTAL PROCEDURE

3.1 MATERIALS

3.1.1 Coal Samples

The coals samples tested were usually run-of-mine (RoM) samples delivered by companies upon our request. Table 1 gives some characteristics of the main coals studied in this project.

3.1.2 Chemicals

All chemicals used were of analytical grade. The concentrated acids, such as sulfuric acid (98% pure), hydrochloric acid (37%), nitric acid (70%) and hydrofluoric acid

Table 1. List of the Coals Selected for the Study

Coal	RoM Ash%	Washed Ash%	Floated Ash%	Supplier
Pittsburgh #8	25	18	6.5	
Splashdam	40	35	6.0	Wellmore Coal Corp., VA
Widow Kennedy	30.5	--	8.2	Wellmore Coal Corp., VA
W K Dominion #1	45	--	3.5	Jewell Smokeless Coal Corp., VA
W K Winston #9	35.4	26.4	--	Jewell Smokeless Coal Corp., VA
W K Coking Coal	--	--	5.4	Jewell Smokeless Coal Corp., VA
Wyodak Anderson	4.0	--	--	Kerr McGee Coal Corp., WY
Jacob's Ranch	11.5	9.0	--	North-Dakota Univ., ND
Jacob's Ranch	10.0	7.0	--	Kerr McGee Coal Corp., WY

(49%), were purchased from Fisher Scientific Company. Ferric sulfate $[\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}]$ from Eastman Kodak was used as an extraneous source of ferric ions.

3.2 EQUIPMENT

3.2.1 Sample Preparation Equipment

For size reduction, a Deco jaw-crusher was used, followed by a hammer-mill from American Pulverizer Company. The coal was then ground in ceramic ball mills, 10 and 15 cm in diameter, using 25mm carbon steel balls.

Standard testing sieves from the Fisher Scientific Company were used to obtain different size fractions. A vibrating shaker by Sepor Inc. helped to wash coal with tap water and to efficiently drain the water.

A Denver D12 laboratory flotation machine, with a 7 liter cell was used to preclean some of the RoM coals. Coarse coal particles were separated from shale with the column shown in Figure 6.

3.2.2 Sample Processing Equipment

Figure 7 shows the double-jacketed vessel, used for the CECC process. It was specially built by Ace Glass Inc. with the following dimensions: 103mm I.D., and 85mm in height. A second cell, only 65mm in height, was used for separate electrolysis (refer to the section 3.3). Heating was provided by a circulating water bath (Endocal Neslab, model RTE 8). The coal slurry was stirred by a teflon-coated magnetic bar, 50mm long and 10mm wide, rotated by a stirring plate such as the Fisher Thermix model 120M or the hot plate 310T. This stirring bar was engaged to avoid significant breakage of particles. Alternatively, a glass impellor with 55mm diameter was also used to stir the coal

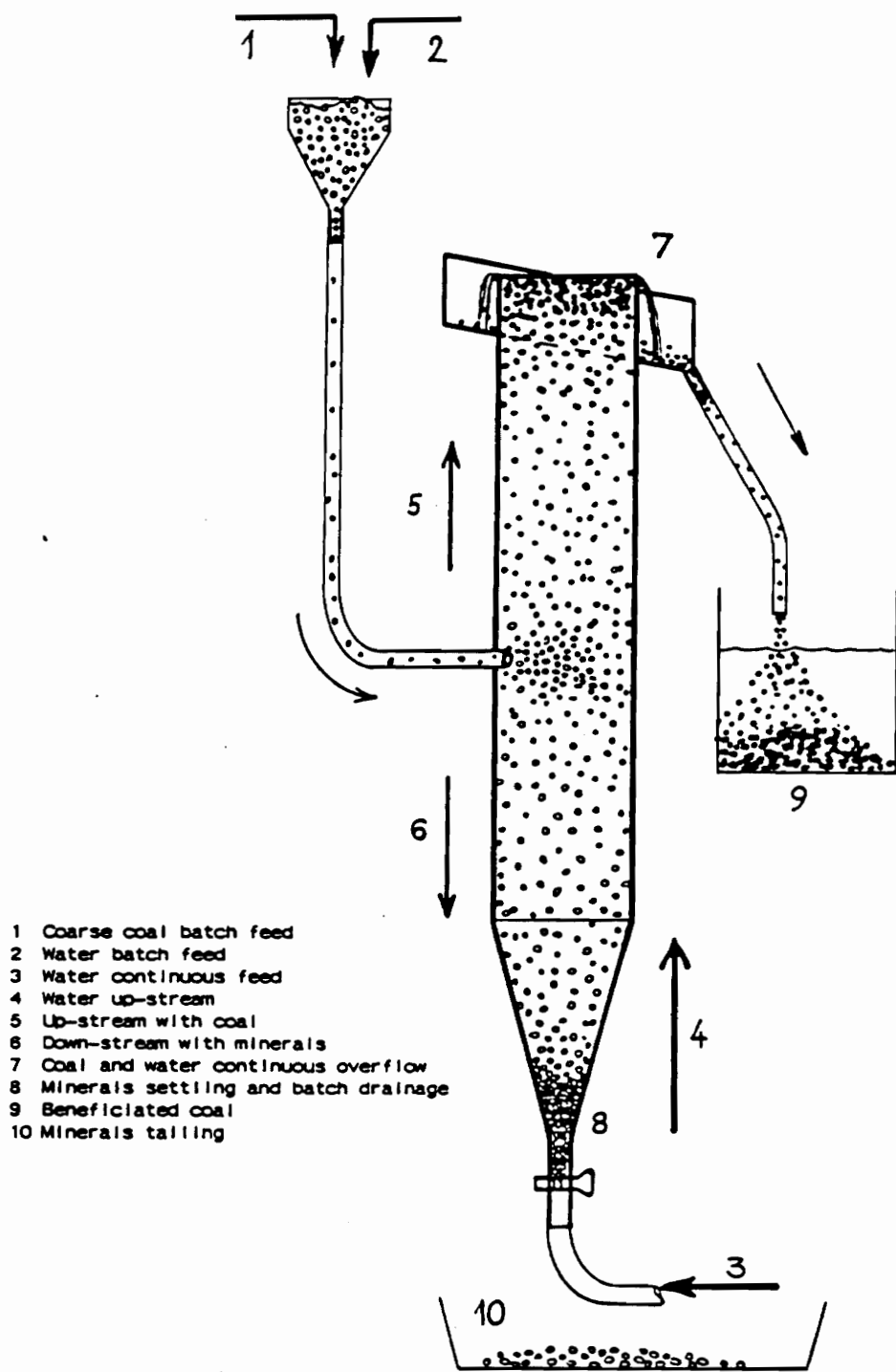


Figure 6. Representation of the Separation Column for Coarse Particles

slurry. During experiments, a 20ml slurry was sampled by means of a syringe, and the slurry could be filtered using a Whatman #44 filter paper.

Each electrode was made of a platinum cylindrical mesh, 25mm in diameter and 50mm in height, and whose surface area was 82cm². The working electrode was immersed in the slurry through the top of the vessel, and communicated to the reference electrode via a Luggin capillary. The counter electrode was placed in a compartment communicating with the slurry through a glass frit. The reference electrode was a Fisher saturated calomel electrode filled with saturated KCl. Potentials necessary for the oxidation of ferrous ions to ferric were supplied using a Scanning Potentiostat 362 made by EG&G Princeton Applied Research. Measurements of the current and charge were made by a EG&G PARC model 379 Digital Coulometer.

The redox potential of the slurry (Eh) was measured by means of a Fisher platinum Ag/AgCl combination electrode, using a Keithley 642 electrometer. The pH was measured by a pH electrode linked to a Cole-Parmer Chemcadet pH-meter.

In order to minimize the chances for breaking the coal particles by the stirrer, a fluidized-bed column was designed as shown in Figure 9 on page 44. The column was sold by Ace Glass Inc., and was 25mm I.D. and 450mm in height. Teflon stoppers holding a glass frit were set at both ends, so that coal particles could remain trapped inside the column. A Cole-Parmer Masterflex peristaltic pump (variable speed) driving a #18 head was used to pump the electrolyte into the column.

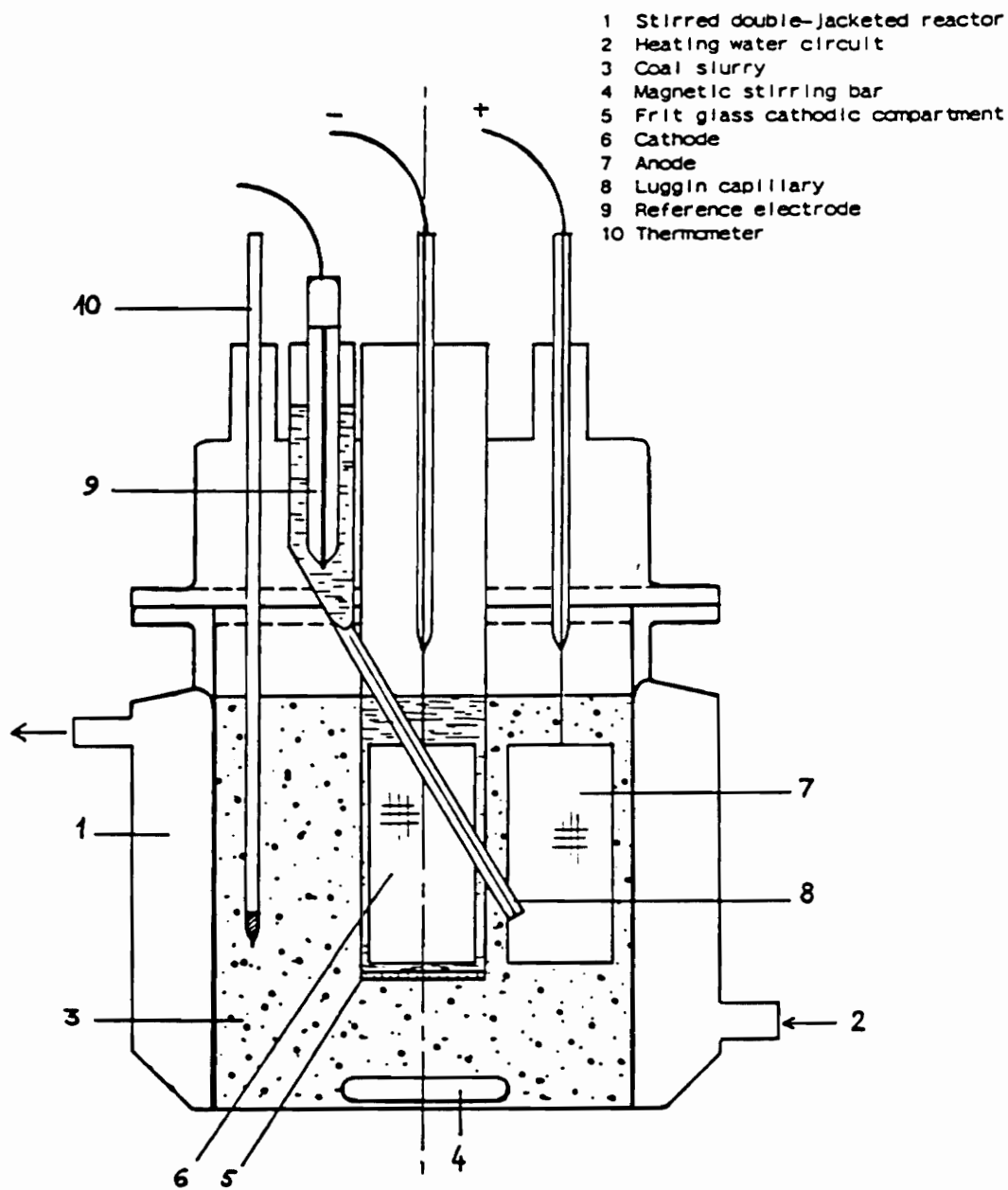


Figure 7. Representation of the Reaction Vessel

3.2.3 Analysis Equipment

Bulk samples were weighed on a Ohaus 1500D balance, and small amounts, on a Mettler AC 100 scale. A Hevi-Duty Electrical Corp. furnace was used for ash analyses. Sulfur analyses were made using a Leco SC 132 sulfur determinator.

Low temperature ashing was done by slow oxidation of coal in the oxygen plasma induced by a LFE Corp. LTA-302 oven coupled with an Alcatel vacuum pump. The low temperature ashes (LT ash) were analyzed by using a Picker Nuclear Diffractometer, using the Cu K- α radiation.

A Cambridge scanning electron microscope Stereoscan 120, was used to take the electron micrographs of the test samples. Sample surfaces were gold-coated using a Denton Vacuum Desk II sputter coater. The Kevex Ray energy dispersive x-ray microanalyzer was able to identify the elements of a mineral by a high energy electron beam.

3.3 PROCEDURE

3.3.1 Sample Preparation

The coal was first crushed to minus $\frac{1}{2}$ inch, and passed through a hammer-mill. The sample was then ground in a ball-mill for 15 min. to obtain minus 40 mesh (380 μm) material. The pulverized coal was dry-screened for 20 minutes on a Rotap to obtain desired size fractions. In some cases, the dry-screened sample was wet-screened to re-

remove small coal and mineral matter particles adhering to the surface. The need to remove these impurities from the feed is obvious; otherwise the fines reporting to the underflow fraction after the CECC process might be mistaken as liberated mineral matter. To ensure complete removal of mineral matter, the coal sample was washed on a vibrating sieve with a water spray for 5 minutes, until the drain water was clear of any fines.

Some of the run-of-mine coal samples assayed too much ash to be treated chemically; there was no advantage in processing free mineral particles since they will simply consume the reagents. Therefore, a substantial portion of the free minerals were removed by flotation from the coal sample before subjecting it to the CECC process. Typically, about 300g of coal was mixed in 6 liters of tap water in the flotation cell, stirred at 1800 rpm. Dow frother M150 was added (one or a few drops) and after one minute, air was introduced to the cell and bubbling was initiated. The coal concentrate was collected at the top, while the depressed minerals remained at the bottom of the cell. The concentrate was refloatated several times until the required purity of feed was obtained. The final concentrate was rewashed on the vibrating screen in order to rinse out the frother and the last fines. It was then dried overnight in an oven (80°C), and stored for later use.

Before and after each test, the feed and the product were riffled to obtain representative samples for assaying. For most tests, three assays were done and averaged.

3.3.2 General Care

Due to the use of hazardous chemicals, glassware, hot fluids, ovens, grinders, etc, extreme caution was taken during each experiment. All the electrodes were stored in

water after use; and the coal samples were stored in the freezer to minimize oxidation. Samples, including coal, ash and low-temperature ash, and hygroscopic reagents such as ferric sulfate were stored in dry atmosphere.

3.3.3 Processing

The process described below has been inherited from Paul's work (1988) on electrochemical tests, and parts of the equipment used were the same. However, the complete procedure and improvements in the system described below are the results from the author's own work.

3.3.3.1 Setting

Acids were mixed and diluted with single distilled water, and the mixture was heated in the reaction vessel at the required temperature. A circulating bath allowed to maintain a very constant temperature in the double-walled jacket of the vessel, as measured by a mercury thermometer. The coal slurry was agitated at a constant rpm (about 800rpm) during the test. The cathode was placed in its fritted glass compartment, while the anode and the luggin capillary were immersed in the slurry. The reservoir of the capillary was partially filled with the electrolyte to create an ionic bridge between the anode and the reference electrode. The reference electrode was tightened in it to keep the liquid from draining. The reference electrode was filled with a KCl 4M saturated solution. The electrodes were connected to the potentiostat which was set usually at 1 volt SCE, and the current was monitored. The coulometer was also connected to the system to monitor the charge passed.

3.3.3.2 Starting the Test

The coal sample to be treated was weighed and added into the acid mix, then stirred strongly to allow slurry to form. At this time, the stop-watch was switched on. The rpm speed of the stirrer was then adjusted and the cap was placed to cover the cell.

After a set period of soaking time, the potentiostat was switched on to provide a potential of 1 volt SCE, and the current was monitored by means of a coulometer. The intensity of the current was maximum when the reaction started, and then decreased continually until a limiting current was reached after a few hours.

3.3.3.3 During Processing

The set parameters, temperature, stirring speed and applied potential, were regularly checked during the test. When samples were collected, appropriate readings such as current, coulometer reading and potential were recorded.

In some tests, 20ml of slurry samples were taken intermittently during the experiment. The sample was poured onto a screen (stainless steel sieve) and rinsed with tap water for 5 minutes. The sieve size was chosen to correspond to the lower size limit of the feed coal. Sometimes, smaller screen apertures were chosen, so that coal particles which had been slightly reduced in size could be retained. The product coal was then poured into a petri-dish and dried in the oven at 80°C. When it was desired to analyze the solution, the sample was poured onto a filter paper held by a funnel. The filtrate was directly bottled for further elemental analysis, while the residue was rewashed with tap water.

3.3.3.4 After Processing

As soon as processing time was over, the test was interrupted. Last readings were made such as temperature, current and coulometric charge. All apparatus were turned off and the slurry was poured out on a sieve and rinsed under a tap water stream for 5 minutes. All the underflow was collected into a bucket, and allowed to settle, so that water could be removed by siphoning, and the underflow collected into a petri-dish for drying.

3.3.4 Analyses

Various types of analyses were conducted on samples, before and after processing, on both solid and liquid phases, in order to monitor the changes occurring on the coal sample. These analyses were both qualitative and quantitative in nature, so that the samples could be characterized and the process efficiency could be determined.

3.3.4.1 Ash Content

The process efficiency is mainly expressed by the percent ash of the product coal, which is compared to the percent ash of the feed. The *percent ash* of a sample is defined as the weight percent of matter remaining after coal has been ashed. About 1g of dry coal was weighed in a crucible. This was then put into the ashing oven whose temperature was raised to 750°C, then remained constant for 3 hours before it was slowly brought down and kept at 75°C. The ash left in the crucible was weighed and the percent ash calculated.

In the tests described in the chapters to come, some abbreviations were used in the tables:

- **RoM** refers to the *run-of-mine*.
- The *percent ash* is symbolized by **A%**.
- The *ash percent reduction* (**A% Red**) is defined as:
$$100 \times [A\% \text{ in feed} - A\% \text{ in product}] / [A\% \text{ in feed}]$$
- The *percent ash removal*, designated as **Ash Rem**, refers to the weight of ash in the feed minus the weight of ash left in the product, over the weight of ash in the feed.
- **U'Flow** refers to the *underflow*.

3.3.4.2 Sulfur Analysis

The amount of sulfur removed during the process was evaluated by measurements of the percent sulfur in the feed and in the product. This was given by the Leco sulfur analyzer, by burning about 0.25g of coal in the furnace (1375°C) for one minute. In the tables, **Sulf.%** expresses the *sulfur percent* of the coal.

3.3.4.3 Low Temperature Ashing

Since the coal undergoes a high temperature during the ashing procedure mentioned above, changes in mineral matter composition are expected. First, some mineral elements may have been lost as gases; second, the distribution of mineral matter may have

been significantly modified. Finally, crystal structure may have undergone important transformations.

To prevent these changes from occurring, the coal must be ashed in a low-temperature ashing (LTA) process (Gluskoter, 1965). The organic matrix was removed by a radio-frequency induced oxygen plasma combustion. The LTA was carried out on RoM, feed, product, or refuse coals, and the ash products were analyzed by x-rays diffraction, SEM and atomic absorption spectroscopy.

About half a gram of fine coal spread on a petri-dish was placed into the LTA oven. Vacuum was set at 0.3 mmHg and oxygen was blown into the cell so that overall pressure did not exceed 0.4 mmHg. Then, the radio-frequency emission was initiated at 250 W. A blue colored plasma appeared, that had turned violet when the reaction was completed after one to three days. It was necessary to interrupt the process every 8-10 hours to better expose the remaining coal to the plasma.

3.3.4.4 *Elemental Analysis*

For elemental analysis, LT ash was digested in a strong acid mix, including hydrofluoric acid, and the filtrate was analyzed by atomic absorption. This provided the concentration of the major elements dissolved. Filtrates of samples were collected during experiments to study kinetics of dissolution of mineral matter.

The digestion of mineral matter was carried out in a teflon beaker containing equal volume of pure HCl and HNO₃. A hot plate was used to maintain gentle boiling conditions, while the mix was stirred with a teflon magnet bar. Splashing was prevented by a polypropylene top covering the beaker. After the soluble minerals were digested, the top was removed and the acid mix was allowed to concentrate by partial evaporation. Then, 20 ml of hydrofluoric acid were carefully added into the beaker after the hot plate

was turned off. The beaker was covered again, stirring was started, and continued overnight to achieve total dissolution of the silicates. The acid mixture was, then, centrifuged to separate the leachate from the remaining solids (mostly coal that had not burned during the LTA), and the liquid was collected, diluted, and sent for analysis. The residue was rinsed with double-distilled water, then put to dry on a dish in the oven before being weighed. Since silicon volatilizes from the solution with fluorine, forming $\text{SiF}_4(\text{g})$, the mass balance for Si may not be very accurate.

3.3.4.5 Scanning Electron Microscopy

Particles of run-of-mine, feed, product or tail were observed with the the SEM which revealed the topography of the surfaces. Differences in reflectivity, in the back-scatter mode, indicated the presence of crystalline substances which are much brighter.

The energy dispersive x-ray microanalyzer coupled with the SEM was used to characterize minerals by providing a spectrum made of peaks corresponding to the specific energies of every element of the shot area. Only typical photographs (electron micrographs) were taken, i.e. pictures of characteristic particles in representative situations shot with the ideal orientation. This helped figuring out the different mechanisms of mineral matter removal involved in the CECC process.

3.3.5 Alternative Processes

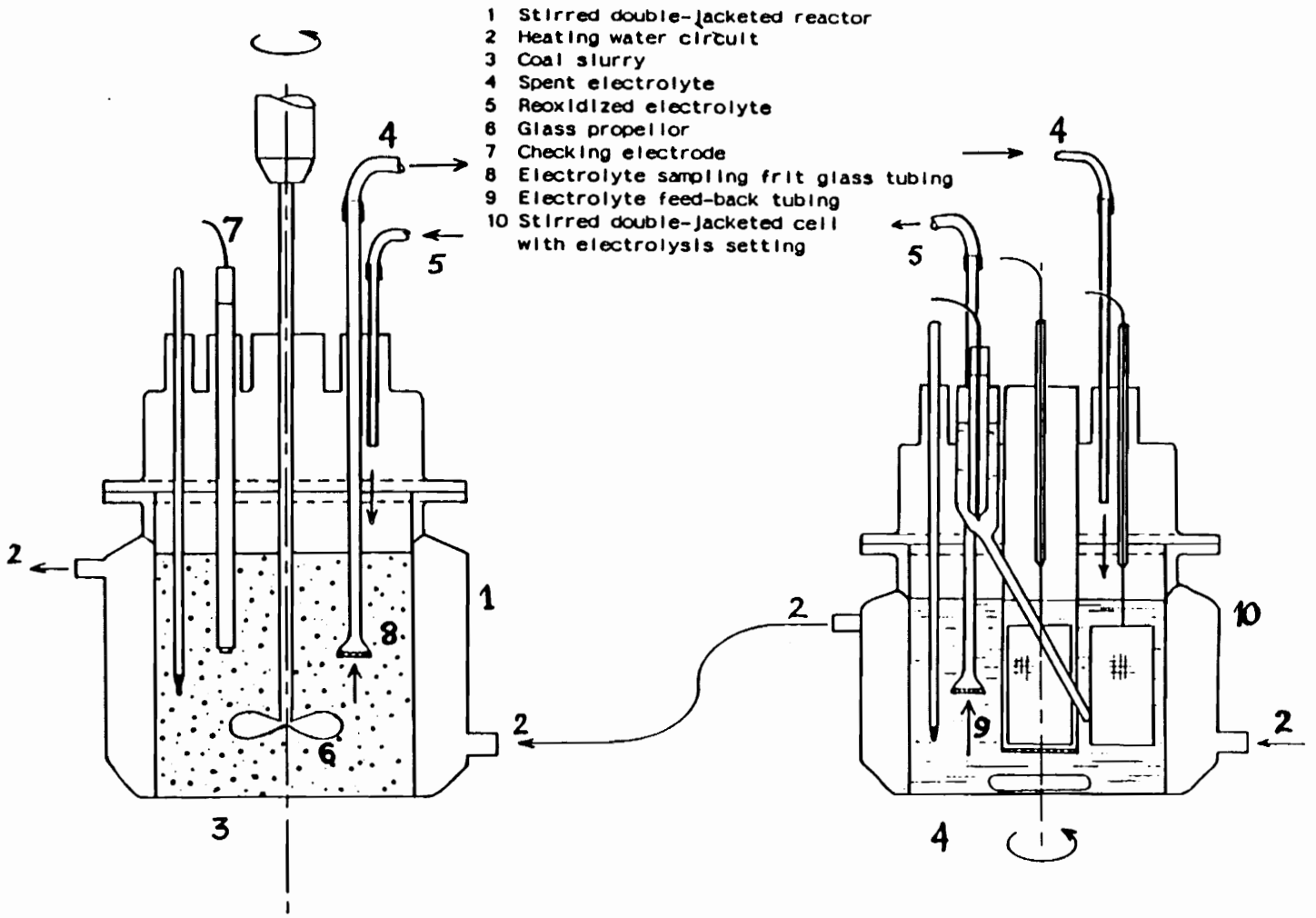
3.3.5.1 *Oxidation in a Separate Reactor*

An alternative way of conducting the CECC was to regenerate Fe^{3+} ions from the spent Fe^{2+} ions separately from the slurry contained in the reaction vessel. The electrode system was placed in the smaller cell. The electrolyte from the reaction vessel was continuously pumped out through a fritted glass tubing, and was sent to the small stirred electrolysis cell. The Fe^{2+} ions were oxidized to Fe^{3+} ions at the anode and the solution containing Fe^{3+} ions was pumped back to the reaction vessel where they were contacted with coal. This is represented in Figure 8.

3.3.5.2 *Elutriated Column*

Figure 9 shows an elutriation column, in which a coal sample is contacted with ferric ions. The spent solution is sent to an electrolysis cell, in which Fe^{2+} are converted to Fe^{3+} ions by contacting with the anode at 1 volt SCE. The electrolyte solution containing Fe^{3+} ions is, then, pumped to the bottom of the elutriation column, which supplies Fe^{3+} ions to the coal and at the same time keeps the coal particles in suspension. This reactor has been designed to eliminate mechanical agitation which may result in size reduction.

Figure 8. Representation of the System for Separate Oxidation of the Solution



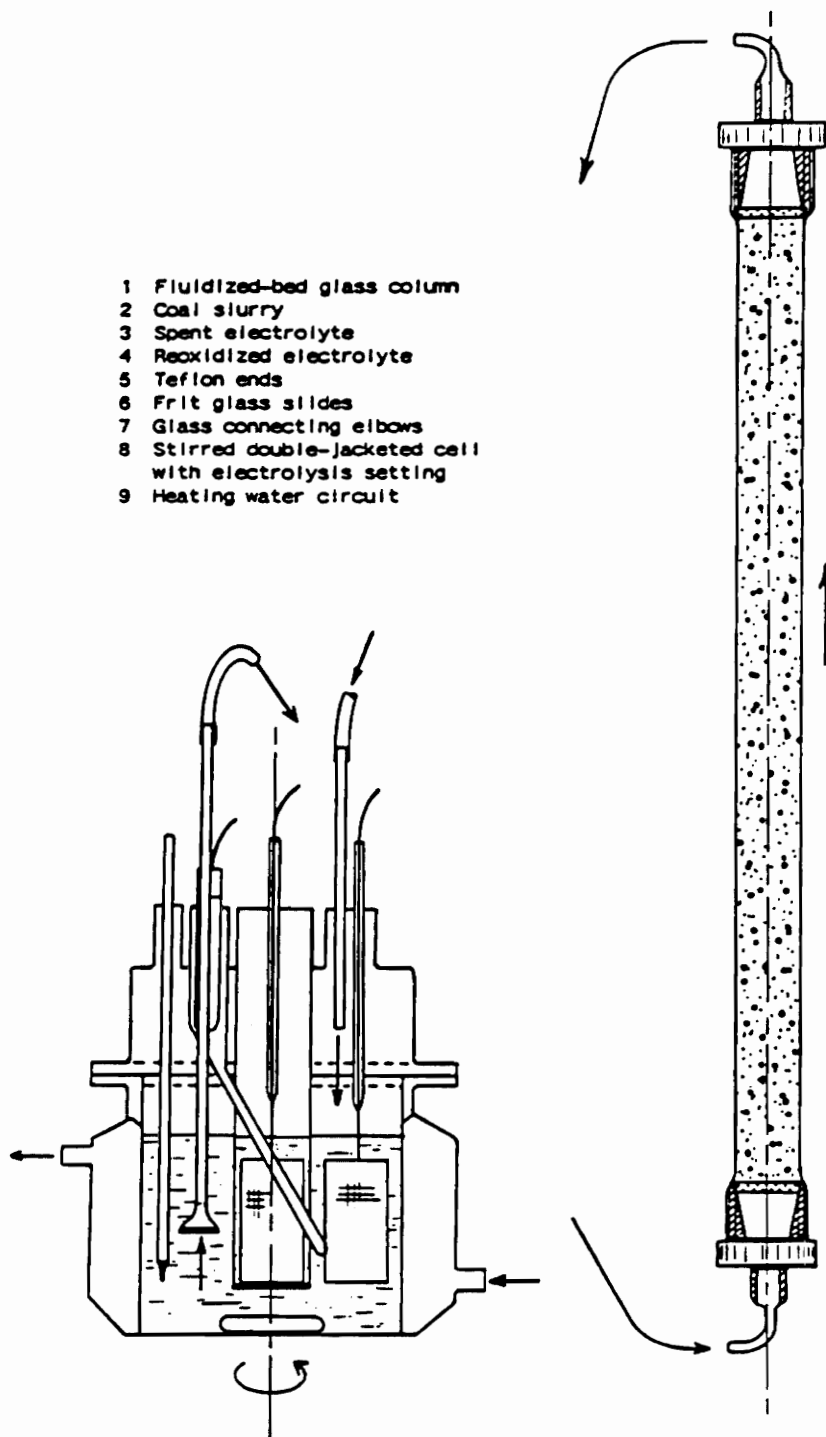


Figure 9. Representation of the Elutriated Column

4.0 TESTS and DISCUSSION

4.1 TESTS on DIFFERENT TYPES of COAL

4.1.1 Pittsburgh #8

4.1.1.1 Tests on Washed Coal

The samples were ground, dry-sieved and washed to remove fines prior to conducting CECC tests. Effect of particle size and reaction temperature were studied.

Effect of Particle Size

A series of three tests were carried out on samples of particle size 25-75 μm , 75-210 μm and 210-840 μm . The operating conditions were as follows: a 51g coal sample was placed in 830ml of 4M sulfuric acid and processed for 5 hours at 55°C, while applying a potential of 1 volt SCE. The reaction product of each size fraction was collected on

a 25, a 62 or a 210 μ m sieve, and washed. However, in order to catch the particles broken during the reaction, finer sieves (38 and 150 μ m.) and filter paper (Whatman #44) were also used to wash the product. The results obtained are given in Table 2.

Table 2. Effect of Particle Size on Ash Removal from Washed Pittsburgh #8

Size (μ m)	RoM Feed A%	Washed Feed A%	Product Ash%	Ash% Reduction	Finer Mesh Prod Ash%
25-75	25.0%	20.5%	11.2%	45.4%	--
75-210	18.3%	15.7%	8.4%	46.5%	10.3% (38 μ m)
210-840	25.0%	22.0%	13.3%	40.0%	20.3% (150 μ m)

The ash reductions achieved were fairly good. The 75-210 μ m fraction proved to be the easiest sample to clean. The product from the 210-840 μ m feed assayed the higher ash content, because the feed contained more mineral matter. The coal products screened on finer sieves proved a higher ash content, because more mineral matter is present in the fine particles. Resoaking the 75-210 μ m product for one hour in fresh water further reduced the ash content, from 8.4% to 7.9%, which is difficult to explain.

Influence of Time and Temperature

Four tests were conducted at 25, 40, 54 and 70°C, with 50g of wet-screened coal (75-210 μ m). For each experiment, the feed was presoaked in 800 ml of 1M sulfuric acid for 5 hours and 10 minutes; then, electrolysis was applied for 5 more hours. 30ml of slurry were sampled after 1/2hr, 1hr, 2hr, 3hr and 4hr, then screened and dried, in order to study the influence of processing time on the CECC. After 5 hours of treatment, the

product was washed and dried for assaying. The results obtained are displayed on Table 3, and plotted in Figure 10 on page 48.

Table 3. Effect of Temperature and Time on Ash Removal from Wet-screened Pittsburgh #8 with Electroleaching

Temp	Feed	A% 1/2h	A% 1h	A% 2h	A% 3h	A% 4h	A% Red	Recov.	Sulf %
25°C	Ash:	--	15.8%	14.4%	14.2%	14.0%	23.5%	70.7%	1.58%
40°C	18.3%	--	13.6%	15.0%	14.7%	12.8%	30.0%	75.2%	1.47%
54°C	Sulf:	13.2%	13.0%	13.2%	11.8%	11.0%	39.9%	81.1%	1.60%
70°C	1.98%	12.0%	12.0%	12.2%	10.2%	9.0%	50.8%	73.3%	1.64%

It is shown that ash rejection improves with increasing temperature. The sulfur rejection averages approximately 20% and appears to be independent of temperature.

4.1.1.2 Physical Cleaning of Pittsburgh #8

The different size fractions of the coal were physically cleaned as follows:

- Froth flotation for the fines ($0-75\mu\text{m}$), followed by wet-screening on a $25\mu\text{m}$ sieve.
- Froth flotation for the medium size ($75-210\mu\text{m}$), followed by wet-screening on a $75\mu\text{m}$ sieve.
- Specific gravity separation for the coarse particles ($210-840\mu\text{m}$).

The results are presented in Table 4, in which **Conc.** refers to the concentrate and **Sulf.%**, to the sulfur content.

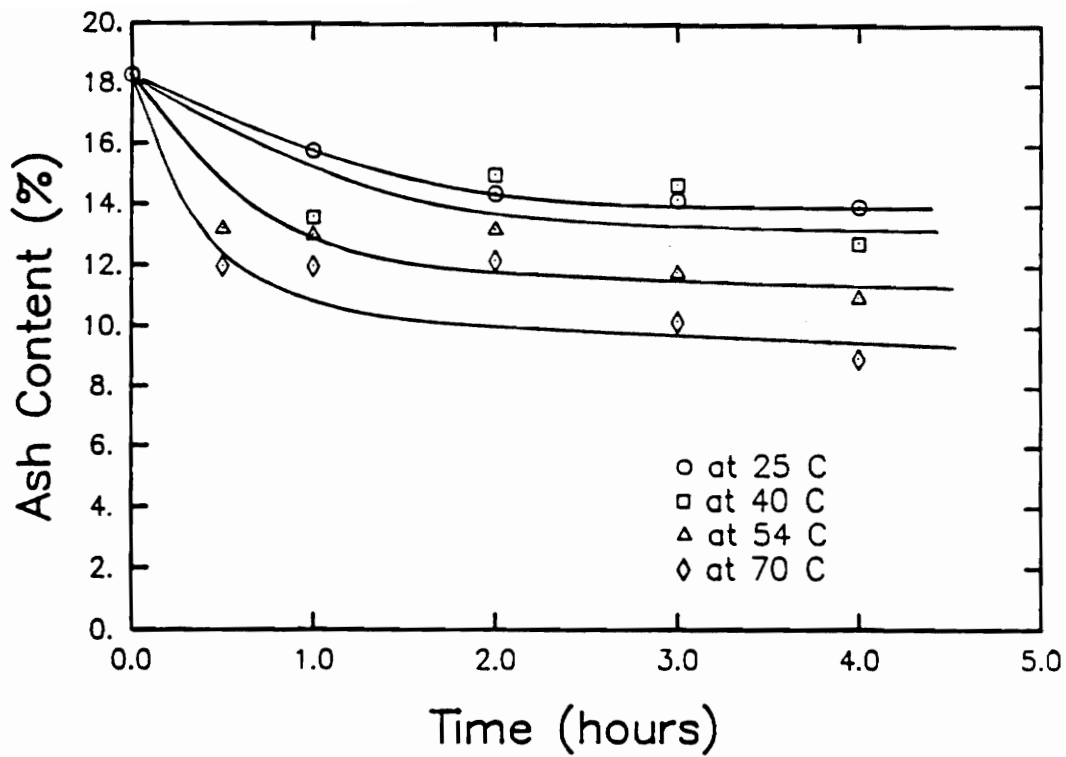


Figure 10. Effect of Temperature on Ash Removal from Wet-screened Pittsburgh #8

Table 4. Physical Cleaning of Different Fractions of Pittsburgh #8 Coal

Size Fraction	RoM Ash%	Washed Ash%	Conc. Ash%	Tail Ash%	Recov.	RoM Sulf.%	Washed Sulf.%	Conc. Sulf.%
0-25 μ m	< 75 μ m	< 75 μ m	12%	< 75 μ m	--	--	--	--
25-75 μ m	24.8%	14.3%	6.78%	78.0%	--	1.65%	2.20%	1.61%
75-210 μ m	24.6%	18.3%	6.50%	47.3%	92.2%	1.61%	1.98%	1.56%
210-840 μ m	25.2%	15.0%	6.57%	77.6%	92.4%	1.57%	1.77%	1.21%

These figures showed significant ash reductions along with good recoveries and fast kinetics. The fact that a mere washing of the run-of-mine coarse coal removed as much as 40% of the ash stresses the phenomenon of adhesion of free minerals on the coal surface. As for fines (minus 75 μ m), the wet-screening on a 25 μ m sieve decreased the ash content by 42%, confirming that fines contain much mineral matter.

Next, the sulfur content of run-of-mine, wet-screened and physically cleaned Pittsburgh #8 increased with decreasing particle size. Furthermore, for all size fractions, the sulfur content increased after the wet-screening of the run-of-mine, implying that sulfur was mostly carried by the macerals. However, the sulfur content decreased after flotation, suggesting that a substantial amount of sulfur was contained in the middlings.

Additional stages of physical cleaning could not yield products with less than 4% ash. This percentage probably corresponds to the mineral matter disseminated throughout the maceral, thus not available for physical removal.

4.1.1.3 Tests on Physically Cleaned Coal

Electroleaching of Physically Cleaned Coal

Four tests were conducted with floated coal (62-210 μ m) at four different temperatures: 28, 42, 55 and 70°C. Each feed, 50g, was dispersed into 800ml of 1M sulfuric acid and processed for 5 hours with an applied electrical potential of 1 volt. Samples were collected after 1, 2, 3, 4 and 5 hours of treatment, and rinsed onto a 62 μ m sieve. The data are reported in Table 5.

Table 5. Effect of Temperature on the Ash Removal from Physically Cleaned Pittsburgh #8 with Electroleaching

Temp.	Feed	A% 1h	A% 2h	A% 3h	A% 4h	A% 5h	A% Red	Sulf %
28°C	6.44%	6.17%	6.17%	6.05%	5.61%	5.68%	13.0%	1.43%
42°C	6.44%	5.84%	5.62%	5.58%	5.43%	5.34%	17.8%	--
55°C	6.44%	5.48%	5.28%	5.17%	5.02%	5.15%	20.8%	--
70°C	7.00%	6.79%	6.36%	5.65%	--	5.18%	26.0%	1.44%

The ash reductions, though limited, were again increasing with temperature; nevertheless, the product ash contents did not vary significantly, and the product could not assay less than 5% ash. The sulfur content was reduced from 1.56% to 1.43%, whatever the temperature.

Simple Leaching of Physically Cleaned Coal

Same conditions as those described in section 4.1.1.3 were used, except that no electrolysis was applied. The results are reported in Table 6.

Table 6. Effect of Temperature on Ash Removal from Physically Cleaned Pittsburgh #8 with Simple Leaching

Temp.	Feed	A% 1h	A% 2h	A% 3h	A% 4h	A% 5h	A% Red	Sulf %
28°C	6.50%	5.81%	5.59%	5.66%	5.61%	5.43%	16.5%	1.42%
42°C	6.44%	6.12%	6.03%	5.66%	5.60%	--	13.0%	--
54°C	6.50%	5.67%	5.46%	5.75%	5.36%	5.68%	15.4%	--
70°C	6.50%	5.95%	5.71%	5.85%	5.51%	5.63%	15.4%	1.44%

The ash reductions were low, and seemed to be independent of temperature. The tailing from the sample treated at 28°C was assaying 7.8% ash only, showing that little mineral matter was liberated. The product sulfur contents were identical to those obtained with electroleaching.

These series of tests demonstrated that CECC conducted with electrolysis slightly improved the mineral matter removal over a simple leaching. Moreover, it revealed that temperature is not an influential factor for further processing physically cleaned Pittsburgh #8.

Influence of Regrinding on Physically Cleaned Pittsburgh #8 Processing

The CECC tests conducted on physically cleaned coal did not produce promising results, which may be attributed to the fact that the mineral matter was not exposed on the surface. Therefore, the physically cleaned coal was reground before treatment by the CECC process. Two series of tests were conducted, involving medium and coarse cleaned coals.

A 180g sample of floated coal (75 to 210 μ m) was reground in the ball mill; its size distribution after grinding is plotted on Figure 11. 28.6g of this coal sample (not wet-screened) was treated in 500ml of sulfuric acid (2M) solution at 55°C for 5 hours and 40 minutes without applying potential (SL), and 4 hours and 30 minutes with applied potential (EL).

Likewise, the coarse coal (210-840 μ m) cleaned by gravity separation, was reground, and then sieved to obtain the range 66-210 μ m. Unlike for the floated sample, the coal (30g) was wet-screened to remove the fines; after drying, 28g remained, indicating that 6.5% were washed away. Next, the sample was mixed with 800ml of 1M (5% sulfuric acid - 4.5% hydrochloric acid by weight of pure acid), and processed at 60°C for 6 hours, both with (EL) and without (SL) applied potential. Results are given in Table 7 and in Table 8.

These results showed that electroleaching did improve the ash removal from the physically cleaned coarse coal that was reground, while less improvement in the ash rejection from the medium size coal was noticed. Moreover, regrinding the feed prior to the CECC could not further clean the products.

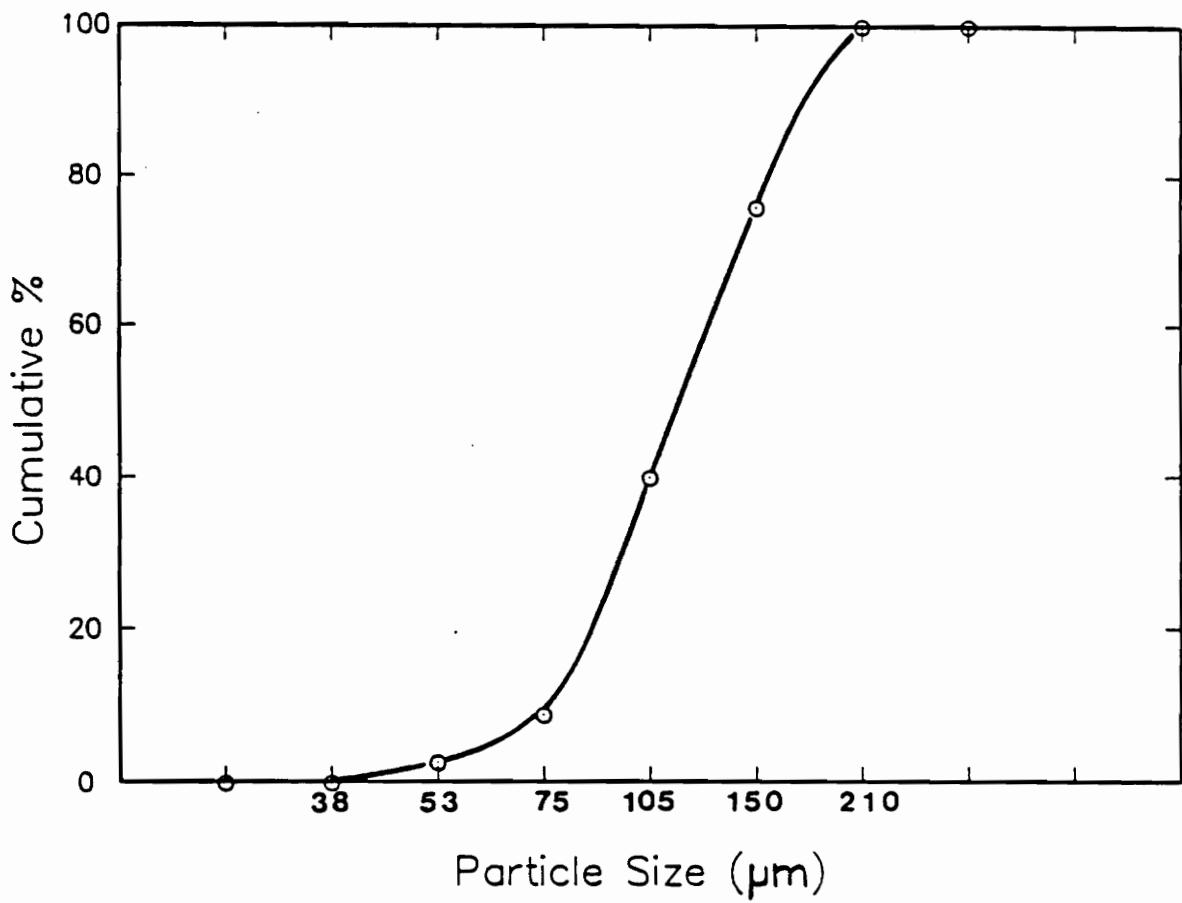


Figure 11. Size Distribution of Physically Cleaned Pittsburgh #8 After Regrinding

Table 7. Effect of Electroleaching on Ash Removal from Reground Medium Pittsburgh #8 Coal

Test	Feed A%	Prod A%	Ash Red
SL	6.39%	5.63%	11.9%
EL	6.39%	6.18%	3.3%

Table 8. Effect of Electroleaching on Ash Removal from Reground Coarse Pittsburgh #8 Coal

Test	Feed A%	Prod A%	Ash Red	Recovery
SL	6.37%	5.49%	13.8%	86.9%
EL	6.47%	5.24%	19.1%	86.5%

Influence of Product Resoaking and Filtration on the Processing

Resoaking the product in fresh water after the test may allow the water to wash out the acid molecules incorporated in the matrix, thus improving the rinsing step. Moreover, resoaking should favor the migration of water toward the inside of the coal pores, and enhance the build-up of osmotic pressure inside crevices or pores. To test this possibility, two tests were conducted using 51g of physically cleaned coal (75-210 μ m) in each test. A 830ml of 4M sulfuric acid solution was used at 55°C for 5 hours with (EL) and without (SL) applied potentials. After the 5 hours of contact with acid, one fourth of the product was water-washed on a 38 μ m sieve, a second fourth was filtered, and the half left was stirred in tap water for half-an-hour, and finally separated using both screening and filtering. The results are given in Table 9.

The results indicate that the product ash contents were further reduced by resoaking. However, EL was not much better than SL which may be attributed to the fact that the acid strength was relatively high (4M). In such a strong acid, simple leaching may remove considerable amount of mineral matter. It is also worth noticing that most filtered products are cleaner than the wet-screened ones, which is difficult to explain.

Influence of Aeration

Considering that ferric ions may play an important electrocatalytic role in increasing coal oxidation, other methods to regenerate spent ferrous ions had to be investigated. An economic way of regenerating Fe^{3+} ions would be simple aeration. To check this possibility, a test was designed in which the electrolyte was pumped out of the reaction vessel, and sent into a vertical cell with fritted glass ends, through which air was blown to oxygenate the liquid. The liquid overflow was then recycled to the vessel. The 50g coal sample (75-210 μ m) was mixed with 800ml of 4M sulfuric acid and processed at 55°C for 6 hours, prior to recovery on a 75 μ m sieve. The data are listed in Table 10.

Table 9. Effect of Product Resoaking and Filtering on Ash Removal from Physically Cleaned Pittsburgh #8

Test	Feed Ash %	Screened Prod A%	Filtered Prod A%
SL	6.50%	5.62%	5.08%
Resoaked	6.50%	5.45%	4.80%
EL	6.06%	5.62%	5.10%
Resoaked	6.06%	5.03%	5.40%

Table 10. Effect of Aeration on Ash Removal from Physically Cleaned Pittsburgh #8

Test	Feed Ash %	Screen Ash %	Tail Ash %	Filter Ash %	Screen Ash Red	Filter Ash Red
Aeration	5.91%	5.15%	7.70%	4.90%	12.9%	17.1%
EL	6.06%	5.62%	--	5.10%	7.30%	15.8%

Although the differences in the results were not significant, the product was slightly cleaner with aeration; therefore, this method may be considered economically viable.

Influence of Ferric Ions

According to the osmotic liberation theory (Paul, 1988), an increase in Fe^{3+} concentration in the electrolyte should improve the oxidation of the coal, and favor the pressure build-up. In order to check this possibility, ferric ions were added to the slurry while a typical test with cleaned Pittsburgh was initiated. A 50g sample of feed coal (75-210 μm) was contacted with 800ml of 1M sulfuric acid solution and with 24.7mM of ferric ions (as ferric sulfate), at 55°C. A 1 volt potential was applied to regenerate the spent ferrous ions into ferric for 5 hours. The results are given in Table 11.

Table 11. Effect of Ferric Ions on Ash Removal from Physically Cleaned Pittsburgh #8

Test	Feed	A% 1h	A% 2h	A% 3h	A% 4h	A% 5h	A% Red
No Ferric	6.44%	5.48%	5.28%	5.17%	5.02%	5.15%	20.0%
Ferric	6.44%	6.08%	6.20%	5.93%	5.41%	5.40%	16.15%

As shown, the extraneous source of ferric ions did not improve the ash rejection. On the contrary, the contents were higher when ferric sulfate was used. This may be explained by the fact that it is not only the concentration of ferric ions that controls the oxidation, but also the ratio between the Fe^{3+} and Fe^{2+} ion concentrations. Furthermore, when a large amount of ferric sulfate is added, considerable amount of $\text{Fe}(\text{OH})_3$ may precipitate out, adding to the ash content. This was likely because the sulfuric acid concentration was low (1M).

4.1.1.4 Statement on Pittsburgh #8 Processing

The various tests conducted on this coal demonstrated the importance of the wet-screening before treatment. It was also shown that wet-screened coal was sensitive to temperature and allowed a considerable ash removal. In some cases, the CECC process with applied potential did not produce markedly superior results as compared to the cases without applied potential. This was usually the case when the acid strength was high (> 4M). At low acid strength, however, results were better with applied potentials than without, although the improvements were rather marginal.

4.1.2 Splashdam

Paul (1988) reported that the CECC process can substantially remove the ash from a Splashdam seam coal. To check the reproducibility, a series of tests were conducted on a Splashdam coal obtained from the Wellmore Coal Corp., although it is not certain that it was from the same mine.

4.1.2.1 Tests on Wet-screened Coal

Preliminary Test

A run-of-mine sample was ground, sieved at 75-210 μ m, and wet-screened. A 48.1g feed sample was then processed in 800ml of 1M hydrochloric acid at 60°C for 6 hours with 1v applied potential. The product was then collected and rinsed on a 38 μ m sieve. Results are given in Table 12.

Table 12. Effect of Electroleaching on Ash Removal from Wet-screened Splashdam

	RoM Coal	Washed Coal	Product Ash %	Ash % Reduc.	Ash Removal	Recov.
Ash	25.0%	23.7%	19.0%	24.0%	28.1%	95.8%
Sulfur	0.65%	0.69%	--	--	--	--

The ash reduction was relatively poor, although the recovery was very high. This may be attributed to the fact that the liberated ash was removed at 38 μ m, rather than at 75 μ m which was the lower size limit of the feed coal. The sulfur content had slightly increased with processing, although no sulphuric acid was added to the slurry, which may be within experimental error.

Influence of Ferric Ions and Electroleaching at High Temperature

Four samples of the Splashdam coal were processed in a series of comparative tests designed to study the effect of electrocatalytic parameters on the ash removal. In the first test, the run-of-mine coal was ground, then sieved in three size fractions and finally wet-screened. Table 13 gives the percent ash of both RoM and washed coals.

The 62-210 μ m fraction was chosen for this series of tests, and 25g samples were processed in 750ml of 1M sulfuric acid at 60°C for 6.5 hours. In case of EL, a 1v potential was applied, 1 hour after the test started. In some experiments, 2mM of ferric ions was added. After the processing, the coal samples were washed with tap water for 5 minutes on a 53 μ m screen. The results are given in Table 14.

Table 13. Effect of Wet-screening on Ash Removal from Run-of-mine Splashdam

Size	RoM A%	Washed A%
0-66 μ m	51.34%	--
66-210 μ m	38.77%	33.38%
210-840 μ m	47.03%	42.08%

Table 14. Effect of Ferric Ions and Electrolysis at 60°C on Ash Removal from Wet-screened Splashdam

Test	Feed A%	Prod A%	Ash% Red	Sulf.%
SL	33.9%	28.6%	15.6%	0.75%
SL + Ferric	33.8%	27.1%	19.8%	--
EL	33.8%	27.1%	19.8%	--
EL + Ferric	33.5%	27.2%	18.8%	0.79%

The results show that although the overall ash rejection did not exceed 20%, the addition of ferric ions improved the ash rejection by approximately 4%. Also, under the applied potential conditions, the ash rejection was improved. These improvements were discernable because the sulfuric acid and the ferric ion concentrations were relatively low.

4.1.2.2 Tests on Physically Cleaned Coal

The 62-210 μ m coal, assaying 38% ash after wet-screening, was subjected to flotation. The concentrate, assaying 5% ash in average, was also treated by the CECC.

Influence of Ferric Ions and Electroleaching at High and Low Temperatures

Two series of tests, at 60°C and at 24°C, were conducted, with simple leaching, simple leaching with ferric ions (2mM), and electroleaching. Every 25g feed sample was mixed in 750ml of 1M sulfuric acid and processed for 6.5 hours. Table 15 and Table 16 show the results.

The results obtained at higher temperature were better, but both EL and ferric ion addition showed no improvement in ash reduction. In fact, at the lower temperature, the Fe³⁺ addition inhibited the process. The reason why no significant ash rejection was observed in these tests was probably because the floated coal did not have much exposure of mineral matter on the surface.

Table 15. Effect of Ferric Ions and Electroleaching on Ash Removal from Physically Cleaned Splashdam at 60°C

Test	Feed A%	Prod A%	Ash% Red
SL	4.90%	4.29%	12.4%
SL + Ferric	5.04%	4.76%	5.56%
EL	5.18%	4.65%	10.2%

Table 16. Effect of Ferric Ions and Electroleaching on Ash Removal from Physically Cleaned Splashdam at 24°C

Test	Feed A%	Prod A%	Ash% Red
SL	5.05%	4.92%	2.6%
SL + Ferric	5.14%	4.76%	7.4%
EL	5.06%	4.83%	4.5%

Influence of Various Parameters at High Temperature

The same floated Splashdam coal was treated in three tests involving different feed ash contents and different operating conditions. The 75-210 μ m fraction samples, each weighing 40g, were used as the feed in three electroleaching tests (potential 1v), in which 800ml of acid was used. The sample was presoaked in the same acid prior to the processing. In test 1 and 2, 1M hydrochloric acid was used, and in test 3, the electrolyte was a 3.2M acid blend made of 15%-13.5% sulfuric-hydrochloric acid (by weight of pure acid), and 20 moles/liter of ferric ions. Each product was rinsed on a 38 μ m sieve. The operating conditions and the results are given in Table 17.

The ferric ions which were used in test 3 did show some improvements as compared to test 2. It seems that at high temperatures, large amount of ferric sulfate addition did not impede the process. It should also be noted that the best ash reduction was obtained with the feed sample containing the largest amount of ash probably because more min-

Table 17. Effect of Various Conditions on Ash Removal from Physically Cleaned Splashdam

Test	Feed Ash %	Presoak. Time	Temp.	Process Time	Screened Prod Ash	Filtered Prod Ash	Ash% Red (Screen)
1	9.74%	3hr	50°C	7hr30	7.60%	7.40%	22.0%
2	5.90%	21hr	65°C	7hr30	5.15%	3.60%	12.7%
3	5.32%	3hr30	65°C	6hr15	4.30%	3.60%	19.2%

eral matter is exposed to the surface. A similar observation was made with washed Pittsburgh #8 coal as well. It is surprising to note that the use of filter paper in collecting the product resulted in better ash reduction than when a screen was used. Similar results were observed with Pittsburgh #8 coal. No proper explanation can be found at this point.

The ferric ions in test 3 did not dramatically improve the process when compared to test 2 or to the experiments conducted so far. Test 3 yielded the cleanest product, which could be due high temperature and very high ferric ions concentration.

The best ash reduction was obtained with the highest feed ash sample in test 1, because more mineral matter was available for removal, like in case of wet-screened Pittsburgh #8. Using filtration, the product ash of test 2 was only 3.6%, which was probably due to the retention of fine minerals in the filter paper.

4.1.3 Widow Kennedy - Wellmore

4.1.3.1 Tests on Run-of-mine Coal

The run-of-mine coal was ground, sieved at 210-840 μ m, and two 25g samples were mixed in a 3.2M acid mixture (15.5%-13.5% of sulfuric-hydrochloric acids by weight of pure acid), at 60°C for 8 hours. Tests were conducted with (EL) and without (SL) applied potentials. The product was collected and rinsed on 3 sieves of different apertures, and analyzed. The results are given in Table 18, in which "Prod" refers to the product collected on the 210 μ m sieve, "Tail 1" the underflow of -210+105 μ m, "Tail 2" the underflow of -105+45 μ m, and "Tail 3" the underflow finer than 45 μ m.. The numbers in parentheses represent the percent weight of product and tails collected in each sieve.

Table 18. Effect of SL and EL on Ash Removal from Run-of-mine Widow Kennedy Wellmore

Test	Feed Ash%	Prod Ash%	Ash% Red	Tail 1 Ash %	Tail 2 Ash %	Tail 3 Ash %	Recov.	Sulf %
SL	30.5%	21.65% (78.8%)	29.02%	52.3% (7.6%)	61.9% (3.2%)	73.7% (5.9%)	88.8%	1.01%
EL	30.3%	21.75% (83.5%)	28.22%	62.2% (5.0%)	73.4% (2.6%)	71.4% (5.1%)	93.7%	1.01%

It is shown that the ash contents of the tails are increasing with decreasing particle size, indicating that the smaller particles are mostly mineral matter. The sum of the tailings represented 16.7% of the total mass collected. The percent ash reduction obtained with and without potentials do not show significant difference, which may be attributed to the high acid concentration (3.2M) and long reaction time (8 hours).

4.1.3.2 Tests on Middlings

The Widow Kennedy coal was physically cleaned by heavy-media separation in a slurry of magnetite, to obtain clean coal of 1 to 5mm in size. The clean coal was re-ground and sieved to obtain the 62-210 μ m fraction, which assayed 8.2% ash. A 25g sample of this mono-size feed was treated in 750ml of the sulfuric-hydrochloric acid mixture 3.2M at 60°C for 6.5 hours in the first stage. In the second stage, 7g of the clean coal from the first stage was treated for 11.5 hours in 600ml of the same acid at the same temperature. In the third stage, the clean coal from the second stage was processed for 11 hours by adding 0.158mM of ferric ions, to the acid solution. The results are shown in Table 19, Table 20 and Table 21.

After the three stages of cleaning, 50% of the mineral matter contained in the feed was removed from the feed. A substantial amount of mineral matter was removed at each stage, even if long processing time was necessary. The results show that under applied potential conditions (EL), the ash reduction was improved. It is most interesting to note that the sulfur rejection was 22% when the potential was applied, for only 4% with simple leaching.

Table 19. Results of the 1st Stage CECC Process Conducted on the Widow Kennedy Wellmore, Coal Cleaned by Heavy Media Separation

Test	Feed A%	Feed S%	Prod A%	A% Red	Ash Rem	Recov.	Yield
SL	8.25%	1.0%	6.56%	20.5%	23.1%	96.7%	98.5%
EL	8.18%	1.0%	6.16%	24.7%	27.3%	96.6%	98.7%

Table 20. Results of the 2nd Stage CECC Process Conducted on the Widow Kennedy Wellmore, Coal Cleaned by Heavy Media Separation

Test	Feed A%	Prod A%	Prod S%	A% Red	Recov.	Yield	Σ A% Red	Σ Yield
SL	6.56%	4.43%	1.06%	32.5%	88.2%	90.5%	46.3%	89.3%
EL	6.16%	3.89%	--	36.9%	90.2%	93.0%	52.4%	91.8%

Table 21. Results of the 3rd Stage CECC Process Conducted on the Widow Kennedy Wellmore, Coal Cleaned by Heavy Media Separation

Test	Feed A%	Prod A%	Prod S%	A% Red	Σ A% Red
SL	4.43%	4.12%	0.96%	7.0%	50.1%
EL	3.89%	3.28%	0.78%	15.7%	59.9%

4.1.4 Widow Kennedy - Dominion #1

4.1.4.1 Test on Wet-screened Coal

The feed sample (53-210 μ m) weighing 40g was mixed in 500ml of the acid mixture H₂SO₄-HCl (3.2M 15.5%-13.5%), and was processed at 60°C for 10 hours with electrolysis (1v). The results of this experiment are shown in Table 22.

Table 22. Electroleaching of Wet-screened Dominion #1

	RoM	Feed	Prod	% Red	U'Flow
Ash	44.0%	43.5%	18.5%	57.4%	50.4%
Sulfur	0.67%	0.72%	1.04%	--	--

Although ash contents were still high, ash reductions were significant. The sulfur content increased, probably because pyrite remained within the macerals while other minerals were removed.

4.1.4.2 Tests on Floated Coal

Processing of a Sample Assaying 7.9% Ash

The Dominion #1 coal, 62-210 μ m in size, was cleaned in two stages of flotation. A slurry of 20g of cleaned coal and 750ml of the 15.5%-13.5% acid mixture was subjected to the CECC process in two stages. The first stage lasted 7 hours and 10 minutes,

whereas the second one lasted 16.5 hours without applied potential, and 14 hours and 20 minutes with electrolysis. The results are given in Table 23.

Table 23. Effect of SL and EL on Ash Removal from Physically Cleaned WK Dominion #1, 7.9% Ash

Test	Feed	Prod A%	Prod S%	Prod A%	Prod S%	Ash %	Sulf %
	A% S%	Stage 1	Stage 1	Stage 2	Stage 2	Red	Red
SL	7.87% A	5.38%	0.86%	4.85%	1.00%	38.4%	7.5%
EL	0.93% S	4.69%	0.72%	3.33%	0.74%	57.7%	22.6%

Widow Kennedy coal again manifested better results with EL, even though temperature was lowered during the second stage due to a circulating bath failure. The sulfur content was reduced by 22.6% with EL, versus 7.5% with SL, which confirmed the observation made with the Widow Kennedy from Wellmore Company. It seems that pyrite rejection is definitely improved by applying the potential. This would underline the role strong oxidant (such as Fe^{3+}) can play, which supports the electrocatalytic mechanism proposed by Paul (1988), as well as the principle of autocatalytic oxidation of pyrite proposed by Lalvani (1986).

Electroleaching of Clean Coal Assaying 3.38% Ash

In the next experiment, a sample cleaner than the one used previously was treated by the CECC to determine how much mineral matter could still be removed. The processing time was shorter than in the previous experiment.

Three stages of froth flotation were conducted on the 53-210 μ m fraction of the run-of-mine coal, and produced a concentrate assaying 3.38% ash. For the test, 22.7g of feed was processed in 500ml of 3.2M H₂SO₄-HCl (15.5%-13.5%) at 60°C for 10 hours and 40 minutes, with the application of a 1 volt potential. The results are given in Table 24.

Table 24. Results of CECC Tests Conducted on the Physically Cleaned WK Dominion #1

	Feed	Prod	% Red
Ash	3.38%	1.66%	50.9%
Sulfur	0.89%	0.71%	21.1%

This test demonstrated that a significant ash reduction could be obtained from a low ash coal already physically cleaned, as well as a fair sulfur reduction. Considering that the major part of the sulfur is from organic origin, 21.1% sulfur rejection may represent almost complete removal of pyrite. Since the run-of-mine coal was assaying 43.5% ash, the overall ash removal, combining physical cleaning and CECC, amounted to 96.2%. As shown in this example, the value of CECC process may not be found in cleaning a RoM coal, but further removing both ash and sulfur from physically cleaned coals.

Electroleaching of Physically Cleaned Dominion #1 in the Elutriated Column

A sample of 30g of cleaned coal, at the size 62-210 μ m, was placed inside the column filled with the same acid blend (15.5%-13.5%); the electrolysis vessel was filled with 750ml of the same solution, so that the whole electrolyte reached one liter in volume.

The test was run at 53°C for 7 hours and 10 minutes, with 9.6mM of ferric ions. The electrolysis (1v) was applied for 5 hours 40 minutes. The results are given in Table 25.

Table 25. Electroleaching of Physically Cleaned WK Dominion #1 in the Elutriated Column

	Feed	Prod	% Red	Ash Rem	Recov.	Yield
Ash	3.45%	2.43%	29.6%	31.9%	96.7%	97.7%
Sulfur	0.82%	0.78%	4.9%	--	--	--

The results are not as good as those obtained with the stirred reactor, which may be attributed to the shorter processing time and the lower operating temperature. However, the absence of mechanical agitation might have eliminated liberation by breakage mechanism.

4.1.5 Widow Kennedy Coking Coal

Multistage CECC Under High and Low Oxidizing Conditions

Two comparative multistage tests were designed to study the influence of oxidizing conditions on the ash removal from a metallurgical coal. The coal was wet-screened at the size 53-210µm, which reduced the ash content from 5.24% to 4.64% and the sulfur, from 0.90% to 0.85%. The acid used for both tests was a mixture of 2:1 sulfuric-hydrochloric acids (by volume of pure acid). The potential of the solution was measured using a silver chloride Eh electrode.

Each test was composed of four stages:

- Stage 1: SL of 35g of feed in 500ml of 1M acid at room temperature for 1.5 hour.
- Stage 2: SL of product from St 1 in 500ml of 3M acid at room temperature for 2hrs.
- Stage 3: EL at 1.2 volt of product from St 2 in 700ml of 1M acid at 60°C for 3hrs.
- Stage 4: EL at 1.2 volt of product from St 3 in 700ml of 3M acid at 60°C for 3hrs with 6.71mM of ferric ions.

In the second series of tests, no potential was applied; instead, nitrogen was blown into the solution to prevent oxygen from entering solution. Nitrogen was introduced through a fritted glass tube from the bottom of the reaction vessel at a flow rate of 267 cc per minute. The results are displayed in Table 26 and Table 27.

Table 26. Multistage Processing Widow Kennedy Coking Coal With Electrolysis

	Feed	St 1	St 2	St 3	St 4	Total
Ash %	4.64%	3.88%	(4.25%)	4.03%	3.59%	--
Ash% Red	--	--	8.41%	5.18%	10.9%	22.6%
Sulfur %	0.85%	--	--	--	0.70%	17.2%
Eh (NHE)	0.79v	0.79v	0.74v	0.80v	0.90v	--

Table 27. Multistage Processing of Widow Kennedy Coking Coal Under Nitrogen Without Electrolysis

	Feed	St 1	St 2	St 3	St 4	Total
Ash %	4.64%	4.41%	(4.49%)	3.76%	3.83%	--
Ash% Red	--	4.96%	--	14.7%	--	17.5%
Sulfur %	0.85%	--	--	--	0.84%	1.20%
Eh (NHE)	--	0.78v	--	0.73v	0.83v	--

Since the ash contents after stage 2 were higher than expected, they are given in parentheses. Ash rejection improved significantly when potential was applied or ferric ions were added. The rest potential measurements show that the slurry became more oxidizing as potential was increased (stage 3 without nitrogen blanket). The potential was further increased when ferric ions were added. It is interesting to know that the ash rejection became effective when the potentials were raised sufficiently. In the presence of nitrogen blanket, the potential did not change very much, indicating that the potential is determined not by the oxygen reduction. Then, most likely reactions that determined the potential would be the Fe^{2+}/Fe^{3+} redox couple. Note that the rest potentials measured are close to the equilibrium potential of the redox couple ($E_{sub0} = 0.77v$). It is also important to note that the ash rejection was much improved with electrolysis.

4.1.6 Wyodak Anderson

4.1.6.1 Influence of Temperature with Simple Leaching

The feed was sieved at the size 150-200 μ m, and a 29g sample was processed in 500ml of the 3.2M sulfuric-hydrochloric acid mixture for 5 hours at various temperatures, while taking the samples regularly. It was found that ash contents did not decrease further after two hours. Table 28 shows the results obtained after 2 hours and 30 minutes.

Table 28. Effect of Temperature with SL on Ash Removal from Wyodak-Anderson

Temp.	Feed	Prod A%	A% Red	Sulf %	Recov.
25°C	Ash:	1.58%	60.5%	0.50%	84.7%
45°C	4.0%	1.38%	65.5%	--	--
60°C	S = 0.4%	1.42%	64.5%	--	--

These ash reductions were definitely higher than those obtained so far, and a very clean coal could be obtained after a short reaction time. The best product was yielded at 45°C, and no significant improvement was noticed for higher temperatures. Note that the sulfur content was increased by 25%, which may be attributed to incomplete washing after processing. Fast reaction kinetics suggests that most mineral matter was readily soluble. However, some of the fines removed may be due to liberation and desliming.

4.1.6.2 *Electroleaching of Wyodak Anderson Coal*

A 53-80 μ m size fraction was wet-screened on a 53 μ m sieve. A 37g feed was processed in 750ml of the 3.2M acid mixture (15.5%-13.5% H₂SO₄-HCl) at 58°C for 7.5 hours with 1v applied potential. The feed assayed 5.26% ash, and the product 2.08%; hence an ash reduction of 60.5%, which is equivalent to the previous tests, was achieved. This result also suggested that neither electrolysis, nor high temperature and nor a longer processing time could improve the process. As a consequence, a simple leaching at around 50°C for a short time should be sufficient to obtain a very clean coal.

4.1.7 *Jacob's Ranch Wyodak Coal, from North-Dakota University*

4.1.7.1 *Preliminary Test with Electroleaching*

The sample was first wet-screened to obtain the 75-210 μ m size fraction, which assayed 8.9% ash. A 25.2g coal sample was processed in 750ml of sulfuric acid 0.5M at 60°C for 8 hours and 15 minutes. The potential was applied after 1 hour and 20 minutes of simple leaching. The results are given in Table 29.

Table 29. Electroleaching of Wet-screened Jacob's Ranch (NDU)

Feed A%	Prod A%	A% Red	Ash Rem	Recov.	Yield
8.91%	3.88%	56.5%	61.5%	88.4%	93.2%

The ash reduction was significant, which is similar to the results obtained with Wyodak Anderson. This coal was therefore a good candidate for comparative study comprising EL and ferric ions addition.

4.1.7.2 Influence of EL and Ferric Ions

Four coal samples (29.3g) 62-210 μ m were treated in 750ml of 0.1M sulfuric acid solution. Tests 1, 2 and 3 were conducted at 60°C, and test 4 at 30°C. Test 1 was conducted without applied potential, while test 2 was conducted with 1v applied potential. In test 3, 0.17mM of ferric ions was added and no potential was applied, while test 4 was conducted with applied potential. The ferric sulfate was added after 30 minutes of presoaking. The results are given in Table 30.

Table 30. Results Obtained With the Jacob’s Ranch Wyodak Coal (NDU)

Test	Time	Temp.	Feed A%	Prod A%	Ash Red	Recov.
1	6hr45	60°C	8.48%	4.45%	47.5%	95.7%
2	6hr45	60°C	8.69%	4.40%	49.4%	95.5%
3	7hr50	60°C	8.82%	3.89%	55.9%	96.4%
4	7hr50	30°C	8.27%	4.65%	43.8%	96.4%

The ash removals at 60°C were higher than the one at 30°C, but the recoveries were similar. The best experiment was the leaching involving ferric ions addition, but it should be stressed that this test lasted 1 more hour. The little difference between SL and EL in absence of ferric ions did not allow to draw a definite conclusion.

4.1.7.3 *Electroleaching in the Separate Oxidation Reactor*

A -62+250µm sample was treated in the stirred reaction vessel, but the ferric ions were regenerated in the separate cell. A 20g coal sample was stirred in 750ml of the 3.2M H₂SO₄-HCl mixture (15%-13.5%) at 60°C for 5 hours and 45 minutes. The electrolyte was kept at the same temperature. The results of the process are listed in Table 31.

Table 31. Separate Electroleaching of Wet-screened Jacob's Ranch (NDU)

	Feed	Prod	% Red
Ash	7.70%	3.06%	60.3%
Sulfur	0.42%	0.58%	--

The ash reduction was again similar to the previous ones, although much stronger acid was used. A longer processing time (10 hours) did not improve the product ash, which was contrary to the behavior of Widow Kennedy coals. This again confirmed that these Wyodak coals did not require a long processing time to be cleaned.

Some flotation tests were conducted on this coal with a purpose to compare the efficiency of the chemical process with some physical methods. None of these assays gave good results. Consequently, this coal appeared to be a good candidate for CECC process.

4.1.8 Jacob's Ranch Wyodak, from Kerr McGee

4.1.8.1 Influence of SL and EL Using the Separate Oxidation Reactor

The first test was conducted the same way as the one in previous section 4.1.7.3, except that temperature was set at 56°C. This test lasted 17 hours. Comparative SL and EL experiments were performed, and their results were reported in Table 32.

Table 32. Effect of SL and EL on Ash Removal from Wet-screened Jacob's Ranch (KMG)

Test	Feed	Prod A%	Prod S%	Ash Red	Ash Rem	Recov.	Yield
SL	6.16% A	2.16%	0.59%	64.9%	69.3%	87.5%	91.2%
EL	0.55% S	2.06%	0.61%	66.6%	70.3%	88.9%	92.7%

These results, as encouraging as the previous ones, did not show significant differences between SL and EL. Underflows were fairly clean, assaying with 6% ash, implying that ash rejection by liberation was not significant.

4.1.8.2 *Electroleaching Using the Elutriation Column*

The column was loaded with 13g of wet-screened coal (size 53-210 μ m) and filled with the same 3.2M acid mixture containing 15.5% H₂SO₄ and 13.5% HCl. The slurry was fluidized at 52°C for 6.5 hours, and the electrolyte was sent to the electrolysis cell where a 1 volt potential was applied. The results are given in Table 33.

Table 33. Electroleaching of Wet-screened Jacob's Ranch (KMG) in the Elutriation Column

	Feed	Prod	% Red
Ash	6.35%	2.38%	62.5%
Sulfur	0.55%	0.69%	--

Since very few tailings had passed the screen after rinsing, liberation of mineral matter and coal size reduction must have been insignificant. Meanwhile, the ash removal was again significant, confirming the ability of this material to be cleaned by the CECC. Sulfur again increased by 25%, but the final sulfur content was still acceptable in view of the environment protection rules.

4.1.8.3 *Simple Leaching Preceded by Regrinding in Acid*

The coal was first reground in acid prior to the CECC. Freshly broken ionic solids (like the various minerals in coal) should present highly hydrophilic and fresh polar surfaces, which should attract the ions and dipoles from the surroundings (Leja, 1982).

By wet-grinding the coal in acid, the available sites which would be candidate for ion adsorption from the electrolyte should be attractive to the reagent molecules, so that immediate reaction with mineral matter would take place.

A sample of raw coal (minus 1mm), assaying 6% ash, was wet-screened on a 38 μ m sieve to remove the fines. Next, about 460g of the sample were poured into the ceramic ball mill along with 250ml of 2M acid (8.6%-4.4% sulfuric-hydrochloric by volume of pure acid), 400ml of tap water and a load of steel balls (1 inch in diameter). Grinding continued for 15 minutes, and then the slurry was wet-screened again on the 38 μ m sieve. Then 34g of the coal were subjected to SL in 750ml of the same acid at 58°C for 5 hours. The resulting ash and sulfur contents are given in Table 34.

Table 34. Effect of Initial Regrinding in Acid on Ash Removal from Jacob's Ranch (KMG)

	Mill Feed	Mill Prod	Mill % Red	Test Prod	Total % Red	U'flow < 38 μ m
Ash	6.03%	3.39%	43.8%	2.57%	57.4%	3.66%
Sulfur	0.55%	0.66%	--	0.73%	--	0.95%

The ash reductions were similar to the previous ones, while the sulfur content was dramatically increased (by 73%). This was probably due to the adsorption of sulfate molecules onto the polar sites. In spite of the theoretical interest of this test, this experiment did not yield a better result.

4.2 EXPERIMENTAL DESIGN for JACOB'S RANCH PROCESSING OPTIMIZATION

The Jacob's Ranch coal, mined from a Wyodak seam by Kerr McGee, was at this point the best responding coal as far as reduction of ash was concerned (over 60%). The following section describes an *experimental design* aimed at setting the tests necessary to determine the best operating conditions for mineral removal. The method followed was from Myers (1971).

4.2.1 Experimental Design

4.2.1.1 Introduction

Various parameters such as temperature, percent solids in the slurry, composition and concentration of acid, particle size, reaction time, oxidizing agents or potential, stirring speed and the order of steps, influenced the release of minerals. It was therefore necessary to find which parameters were the most important, and to what extent.

The four parameters chosen were the mass of coal per volume of slurry (X_s), the concentration of ferric ions added (X_f), the acid strength (X_a) and temperature (X_t). The particle size, stirring speed, acid composition and reaction time were kept constant. Furthermore, the procedure only involved simple leaching (SL), since no significant improvement was obtained by EL. Each test was characterized by an input, involving four parameters (X_i) or variables, and by an output, that is the response of the system to the

CECC. The first outputs measured were ash reductions, and the second ones were the concentrations of the elements solubilized in the leachates sampled during each test. The results of the tests will be compared with the theoretical output predicted by the experimental design.

4.2.1.2 Experimental Procedure and Operating Conditions

Based on previous experiments, fair conditions seemed to be 50 grams of feed treated in 750 ml of 2M H₂SO₄-HCl mixture (2-1 by volume of pure acid, that is 8.6%-4.3% by volume) at 50°C and for 4 hours. Therefore, it was decided to make the pulp density, X_s, vary from 20 to 240 g of coal per 750cc of solution, the acid concentration, X_a, from 0.2 to 4 moles, the ferric ions, X_f, between 0 and 13 mM and the temperature, X_t, between 22 and 70°C. The reaction lasted 4 hours. For the 53-180µm fraction, stirring speed was maintained at 800rpm by a glass propeller driven by a motor set above the cell. This stirring avoided any grinding of particles at the bottom of the cell.

Each experimental variable, X_i, was allowed to vary linearly, and at each of the five designed values was ascribed a coded variable (-2, -1, 0, 1 and 2). Table 35 shows the correspondance between the coded variables and the designed experimental values.

A total of 27 tests were necessary to realize all combinations involving the coded variables -1 and 1 (16 tests), the combination of all variables set at 0 (1 test reproduced 3 times), and all combinations with one variable at -2 or 2 and the three others at 0 (8 tests).

All the coal needed (3.5 kg) was ground, sieved, and wet-screened. Before each test, the feed was ashed three times and averaged. Samples were taken after 1/2 hour, 1h, 2h, 3h and 4 hours, and were filtered. Each residue was rinsed and dried, before ash and

Table 35. Levels of the Experimental and Coded Variables for Jacob's Ranch KMG Chemical Cleaning Optimization

Coded Var → Variables ↓	-2	-1	0	1	2
Xs (g/l)	27	100	173.5	246.7	320
Xf (mM)	0	3.33	6.66	10	13.3
Xa (M)	0.2	1.15	2.1	3.05	4
Xt (°C)	22	34	46	58	70

sulfur contents were determined. The filtrates were sent for elemental analysis. The bulk product was collected and rinsed with 7 liters of tap water, then dried for ash and sulfur determination, while the underflow was allowed to settle before being collected and dried in a petri dish.

4.2.1.3 Results

Product ash contents and ash reductions for every test are reported in Table 36. The concentrations of the dissolved elements are provided in appendix A.

The effects of the various parameters were not immediately obvious, except for temperatures. The next section will discuss the determination of the best operating conditions computed by the ash reduction output.

Table 36. Operating Conditions and Responses of the Processing Optimization

Test #	Coded Variables for				Xs (g/l)	Xf (mM)	Xa M	Xt °C	Prod Ash%	Ash% Red
	Xs	Xf	Xa	Xt						
01	-1	-1	-1	-1	75	3.3	1.15	34	3.71%	46.85%
02	1	-1	-1	-1	185	3.3	1.15	34	4.03%	41.68%
03	-1	1	-1	-1	75	10	1.15	34	4.03%	43.56%
04	1	1	-1	-1	185	10	1.15	34	4.29%	38.89%
05	-1	-1	1	-1	75	3.3	3	34	4.26%	38.88%
06	1	-1	1	-1	185	3.3	3	34	3.93%	43.53%
07	-1	1	1	-1	75	10	3	34	4.39%	37.82%
08	1	1	1	-1	185	10	3	34	4.07%	42.11%
09	-1	-1	-1	1	75	3.3	1.15	58	3.44%	51.41%
10	1	-1	-1	1	185	3.3	1.15	58	3.31%	53.31%
11	-1	1	-1	1	75	10	1.15	58	3.57%	48.78%
12	1	1	-1	1	185	10	1.15	58	3.61%	49.72%
13	-1	-1	1	1	75	3.3	3	58	3.29%	50.45%
14	1	-1	1	1	185	3.3	3	58	3.75%	44.53%
15	-1	1	1	1	75	10	3	58	3.31%	53.31%
16	1	1	1	1	185	10	3	58	3.70%	47.37%
17	0	0	0	0	130	6.6	2.1	46	3.64%	46.71%
18	0	0	0	0	130	6.6	2.1	46	3.79%	43.01%
19	0	0	0	0	130	6.6	2.1	46	3.75%	48.06%
20	-2	0	0	0	20	6.6	2.1	46	3.61%	49.65%
21	2	0	0	0	240	6.6	2.1	46	3.52%	47.31%
22	0	-2	0	0	130	0	2.1	46	3.79%	44.26%
23	0	2	0	0	130	13.3	2.1	46	3.56%	48.63%
24	0	0	-2	0	130	6.6	0.2	46	4.21%	39.86%
25	0	0	2	0	130	6.6	4	46	3.80%	44.93%
26	0	0	0	-2	130	6.6	2.1	22	4.33%	37.06%
27	0	0	0	2	130	6.6	2.1	70	3.29%	52.25%

4.2.1.4 Statistical Analysis on the Ash Reductions

Computing and analyses are fully described by Myers (1971). For the care of 4 variables, a response model of the second order (called fitted response surface) will be of the type:

$$AR = B_0 + [\sum_j B_j X_j] + [\sum_j \sum_m B_{jm} X_j X_m] + [\sum_j B_{jj} X_j^2]$$

where:

j and m are integers which vary from 1 to 4,

AR is the ash reduction output given by the test involved,

B_0 is the estimated AR,

B_j are estimated coefficients, and

X_j are the coded variables.

Using the above formula, 27 equations involving the coded variables and the ash reductions of the 27 tests had to be integrated to provide all the required estimators B_j . The tool that allows to compute the response function (fitted second order surface) was a program which inverts matrices and uses the method of least squares (Mehta, 1988). AR was given as a function of X_j ; the stationary point was set with the optimum X_j (called X_0) which maximized AR, that is annulled the derivatives of the function AR by each X_j . The stationary point was:

$$X_s = 1.1565$$

$$X_f = -2.321$$

$$X_a = -1.159$$

$$X_t = 3.9703$$

and the estimated response was $AR = 52.953\%$.

Two of these coded variables being outside the studied area, representing extreme operating conditions, a canonical analysis had to be conducted to fit the variables to the response surface. The canonical form of the response was calculated:

$$AR = 52.953 - 1.045 W_s^2 - 0.4108 W_f^2 + 0.441 W_a^2 + 0.7609 W_t^2$$

where W_i are the canonical variables.

To maximize AR, W_s and W_f have to be nul, whereas W_a and W_t must be maximum. The relationship between the X_i and the W_i was established, and the W_i were

scanned until they could correspond to acceptable values for the X_i (i.e. to vary between -2 and 2).

The optimum canonical variables that fit acceptable X_i variables were found to be: $W_s = W_f = 0$, $W_a = 3$ and $W_t = 0.3$. This corresponded to $X_s = 0.463$ (207 g of coal per liter of slurry), $X_f = 1.419$ (11.3 mM of ferric ions), $X_a = 0.5371$ (2.61 M of acid) and $X_t = 1.041$ (58.5°C). The ash reduction predicted from these canonical variables was $AR = 56.99\%$, which was higher than any experimental AR obtained in the 27 tests. The test "T", conducted under optimum operating conditions gave, however, only 50.36% ash reduction (see also appendix B providing the elemental concentrations).

It was first thought that the model could not predict the correct outcome of the experiment, probably because the operating conditions would have interacted each other in an unpredictable way. It was thus necessary to check the validity of the model, by using other variable levels.

For canonical variables set to $W_s = W_f = 0$, $W_a = 3$ and $W_t = -1.93$, the corresponding coded variables were $X_s = -0.041$ (170 g of coal per liter), $X_f = 1.997$ (13.3 mM of ferric ions), $X_a = 0.8811$ (2.937 M of acid) and $X_t = -1.023$ (33.7°C). The expected response was $AR = 41.9\%$, and the test conducted showed an ash reduction of $AR = 42.71\%$. This fit between predicted and experimental results demonstrated the validity of the model at least under the conditions employed in the present work. The failure in predicting the optimum condition may be attributed to the interactions between parameters such as temperature and acid concentration. In order to identify the interacting parameters, analyses of the dissolved species was conducted.

4.2.2 Effect of Various Operating Conditions on Dissolution

The effect of three parameters, ferric ions addition, acid concentration, and temperature, which were considered to be the most important in the CECC processing of the Jacob's Ranch coal, were studied with regard to elemental release into acid solution. In each of the following tables, the variations of concentration of each element dissolved are expressed by a sign plus [+], nul [0] or minus [-] (or [--]), meaning that the effect of the variation of the parameter was to release more, as much, or less (or much less) of the element, respectively. The effect of the parameters on the ash reductions between the two tests are also reported.

4.2.2.1 Effect of Ferric Ion Addition

The first parameter studied was the amount of ferric ions added to the slurry. Table 37 presents the variations of concentration of the major elements while the concentration of the added ferric ions was varied from 3.3 to 10mM and the other parameters were fixed.

From this table, it is clear that the increase in ferric ions concentration did not affect the elemental release, except for magnesium which was definitely inhibited. As for the ash reduction, it tended to improve when $[\text{Fe}^{3+}]$ was relatively low, which supported the observations made in the experimental design. Therefore, ferric ions did not seem to have a significant role in the mineral matter removal from this coal. This finding is not surprising because the amount of ferric ions added is comparable to the amount of iron released in solution from the mineral matter itself, as will be seen in the following section.

Table 37. Effect of Ferric Ions on the Release of Major Elements from Jacob's Ranch (KMG)

Tests	[Fe ³⁺] (mM)	Feed (g/.75l)	[Acid] (M)	Temp. (°C)	Elements Release					Ash% Red
					K	Al	Si	Mg	Ca	
01→03	3.3→10	75	1.15	34	0	0	0	-	-	-
02→04	3.3→10	185	1.15	34	0	-	0	-	0	-
05→07	3.3→10	75	3	34	0	+	0	-	0	-
06→08	3.3→10	185	3	34	0	0	0	-	-	-
09→11	3.3→10	75	1.15	58	0	+	0	-	+	-
10→12	3.3→10	185	1.15	58	0	-	0	-	+	-
13→15	3.3→10	75	3	58	0	-	0	-	-	+
14→16	3.3→10	185	3	58	0	+	0	-	+	+
20→21	0 →13.3	130	2.1	46	0	0	0	-	-	+

4.2.2.2 Influence of Acid Concentration

In this section, the tests carried out with 1.15M and 3M acid are compared to study the influence of acid concentration on the release of every major elements, iron included. Variations are shown in Table 38 where characteristic tendencies appear.

At low temperature (34°C), the release of Mg, Fe and Al always increased with stronger acid, while at the same time calcium concentration decreased. K and Si were unaffected, if not adversely affected. *At 46°C,* exactly the same trends were observed.

Table 38. Effect of Acid Concentration on Major Element Release from Jacob's Ranch (KMG)

Tests	Increase of [Acid]	Feed (g/.75l)	[Fe ³⁺] (mM)	Temp. (°C)	Elements Release						Ash% Red
					K	Al	Si	Mg	Ca	Fe	
01→05	1.15→3	75	3.3	34	-	+	-	+	-	-	-
02→06	1.15→3	185	3.3	34	-	+	-	+	-	+	+
03→07	1.15→3	75	10	34	0	+	-	+	--	+	-
04→08	1.15→3	185	10	34	0	+	-	+	--	+	+
09→13	1.15→3	75	3.3	58	0	+	0	-	--	-	-
10→14	1.15→3	185	3.3	58	0	-	-	--	--	--	-
11→15	1.15→3	75	10	58	0	-	-	-	--	--	+
12→16	1.15→3	185	10	58	0	-	-	-	--	--	-
24→25	0.2→4	130	6.6	46	0	+	-	+	--	+	+

At higher temperature (58°C), on the contrary, the release of every element was significantly reduced when acid strength increased. Figure 12 and Figure 13 on page 94 give the results of tests 01 and 05, in which 75g of feed coal was used, and Figure 14 and Figure 15 compare the results of tests 02 and 06, in which 185g of coal was used. It is interesting to note that calcium and magnesium concentrations were initially high, but decreased with time. Similar observation was made at low temperature (34°C).

To summarize, at low temperature, an increase in acid concentration did enhance the release of every species but calcium, but at a higher temperature, the dissolution of all species was inhibited with an increase in acid strength. The critical temperature

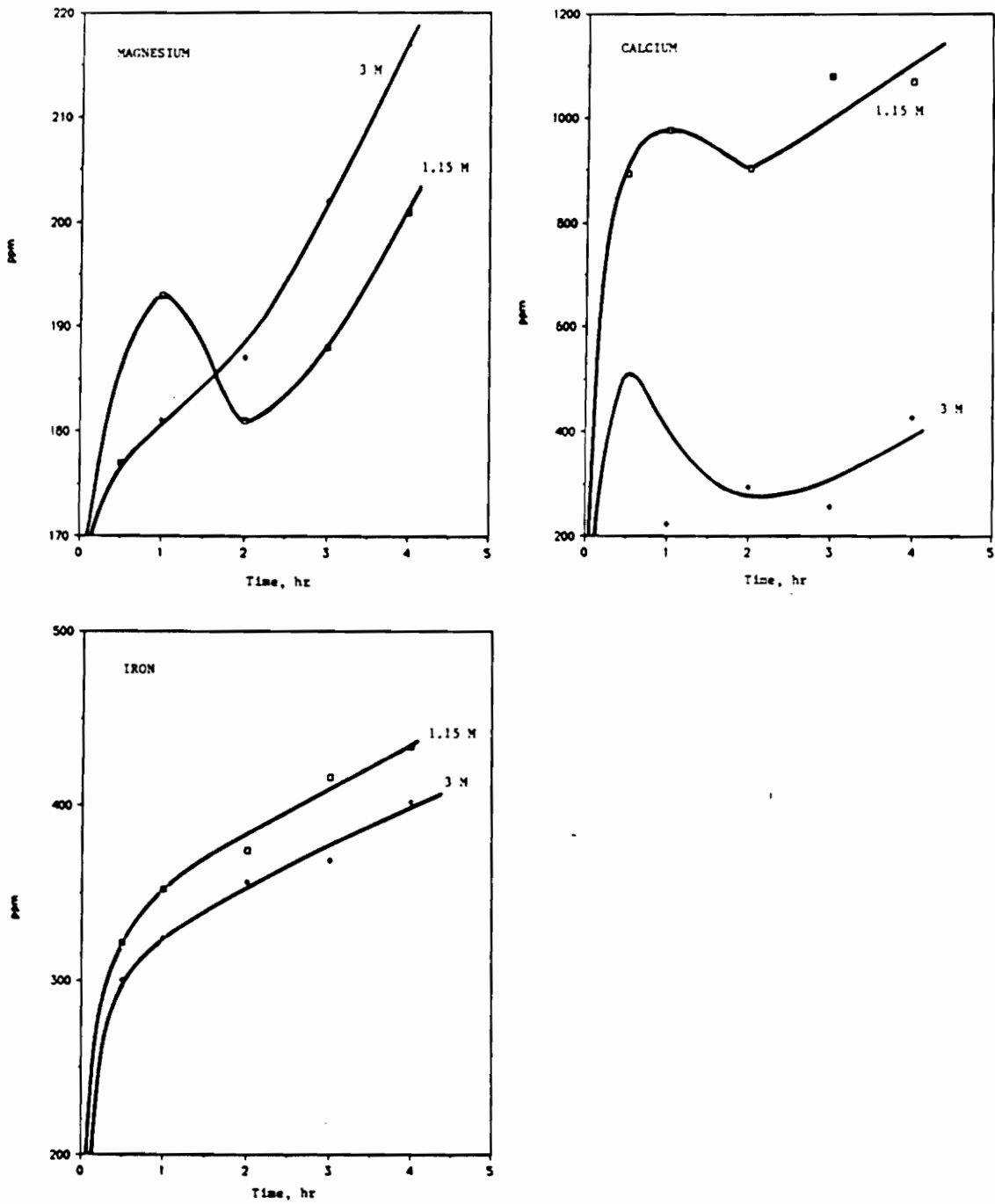


Figure 12. Release of Various Elements in 1.15M and 3M Acid Solutions from Jacob's Ranch Coal (75g) as a Function of Time

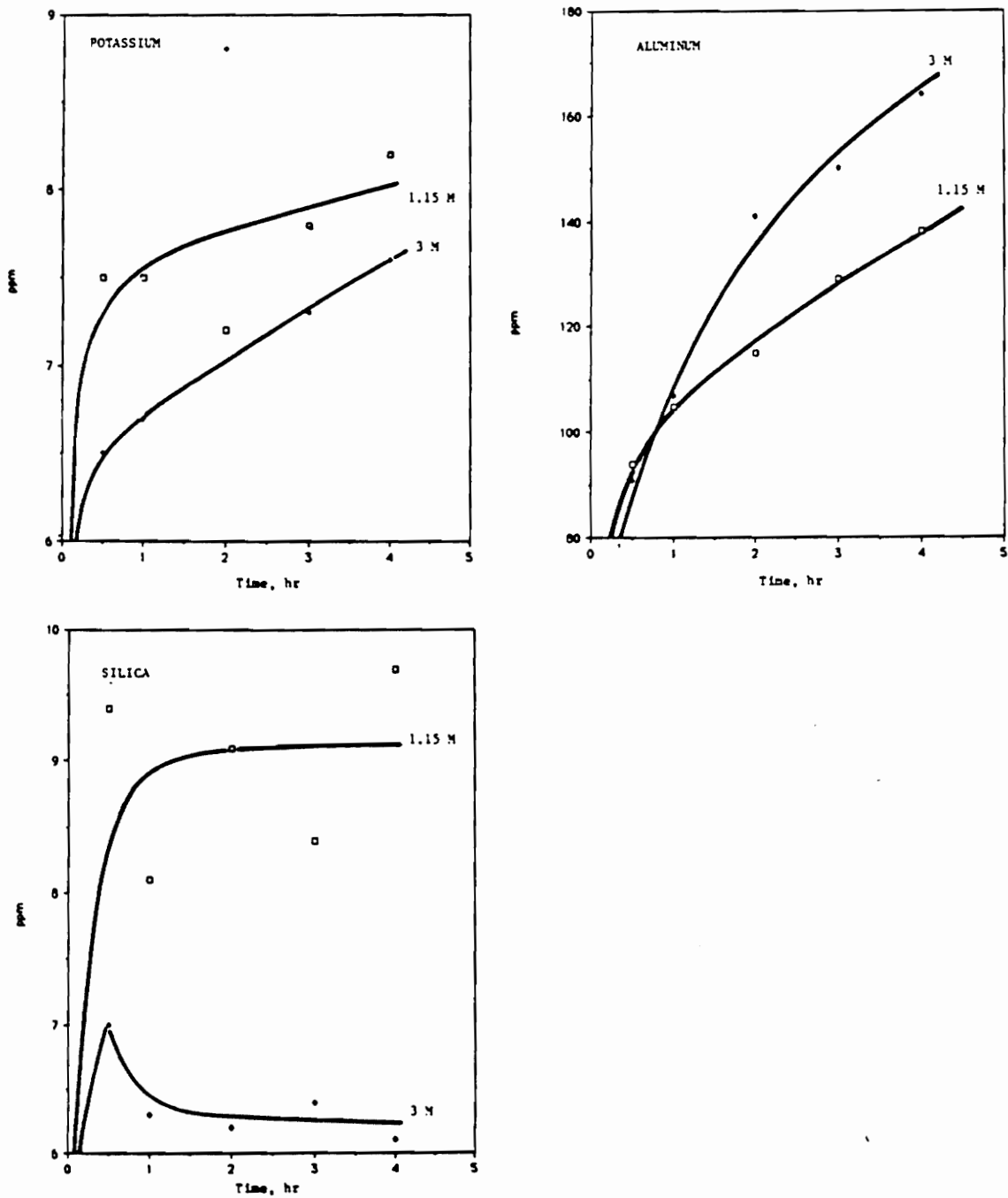


Figure 13. Release of Various Elements in 1.15M and 3M Acid Solutions from Jacob's Ranch Coal (75g) as a Function of Time - *Contd*

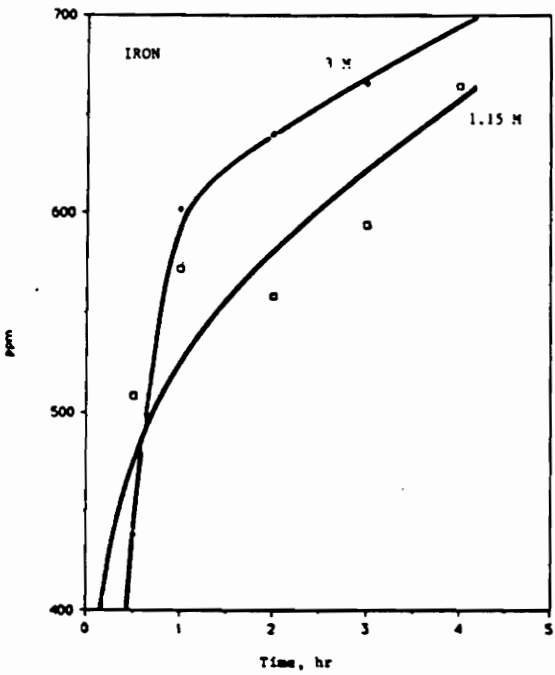
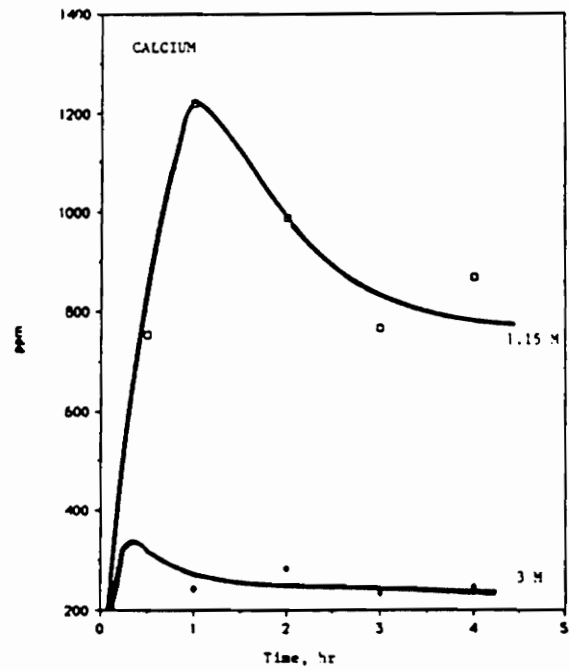
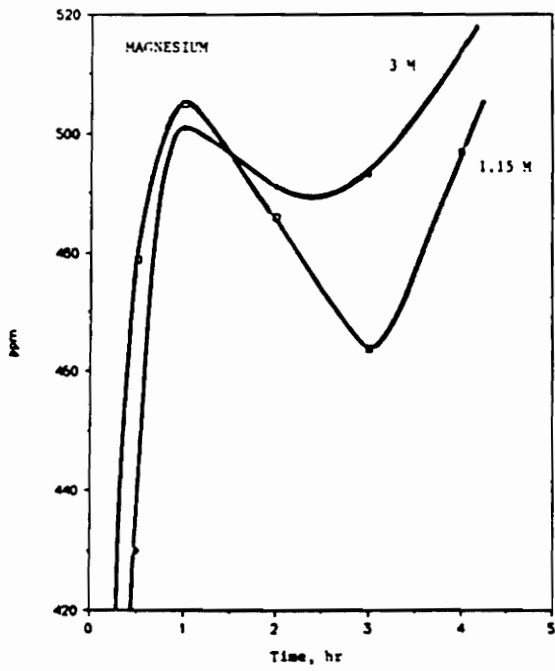


Figure 14. Release of Various Elements in 1.15M and 3M Acid Solutions from Jacob's Ranch Coal (185g) as a Function of Time

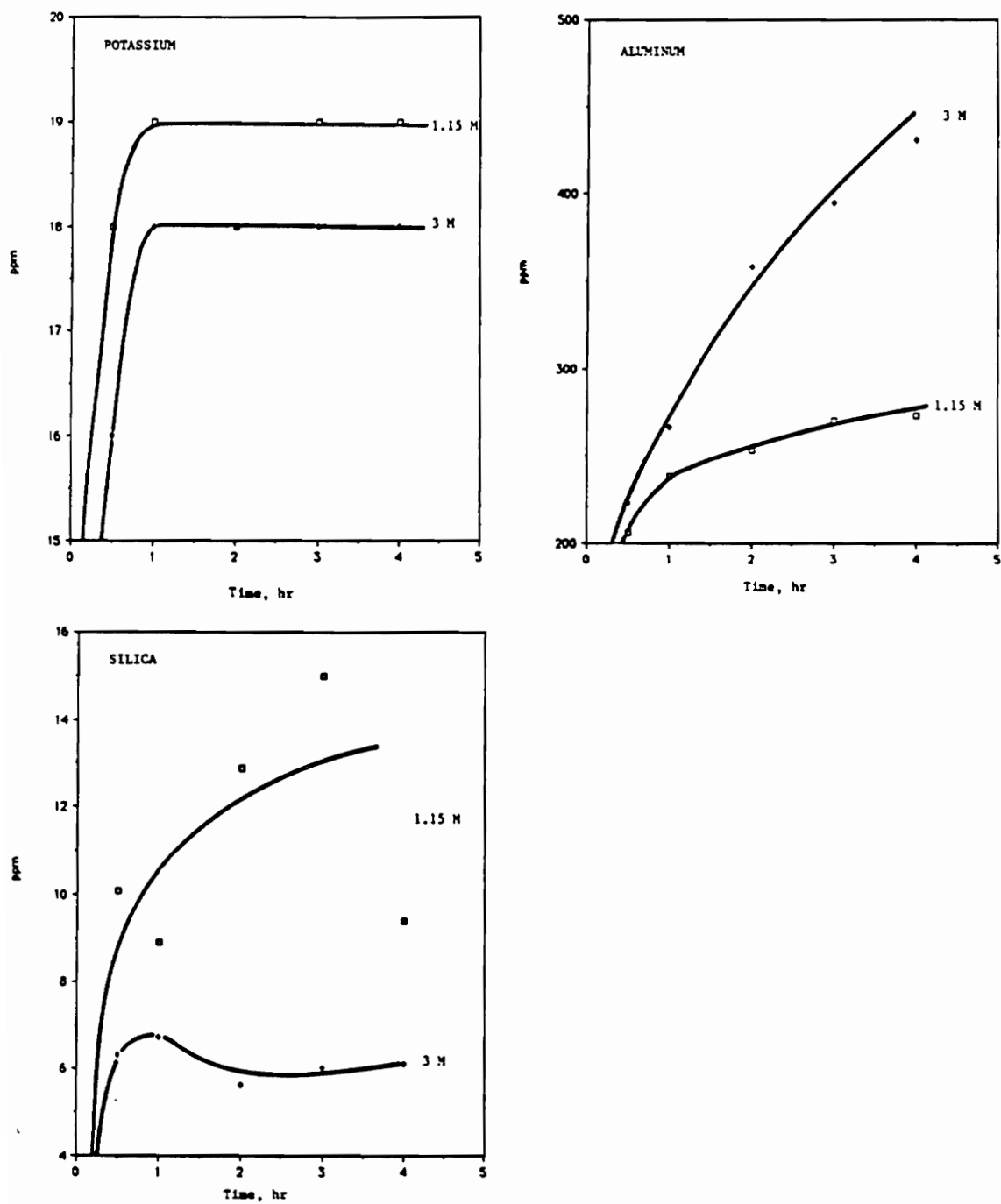


Figure 15. Release of Various Elements in 1.15M and 3M Acid Solutions from Jacob's Ranch Coal (185g) as a Function of Time - *Contd*

seemed to be around 50-55°C. It should therefore be more efficient to use a stronger acid at low temperature, and a weaker acid at high temperature. Precipitation may, thus, explain the unexpected results obtained in the experimental design.

4.2.2.3 *Effect of Temperature*

The last parameter to be studied was temperature. In Table 39, the tests carried out at 34°C are compared with those at 58°C.

On the one hand, calcium and magnesium concentrations were decreasing with increasing temperature, whatever the acid strength may be; but unlike Ca, Mg was better dissolved at 70°C than at room temperature. The inhibition of calcium dissolution at high temperature may be due to the decrease of bassanite solubility in hot solutions (CRC Handbook, 1981), as well as to the precipitation of calcium sulfates such as gypsum, or anhydrite. On the other hand, the release of iron and aluminum increased with high temperature, especially when the acid concentration was not more than 1 or 2M. As for potassium and silica, they dissolved slightly better at low acid concentration than at high concentration (> 2M).

It may be concluded, therefore, that Ca- and Mg-containing minerals do not require high temperature to be dissolved, whereas other metals, especially those forming silicates, pyrite and siderite, are better dissolved at higher temperature, as long as the acid concentration is not too high.

Table 39. Effect of Temperature on Major Elements Release from Jacob's Ranch (KMG)

Tests	Increase of Temp.	Feed (g/.75l)	[Fe ³⁺] (mM)	[Acid] (M)	Elements Release						Ash% Red
					K	Al	Si	Mg	Ca	Fe	
01→09	34→58	75	3.3	1.15	0	+	0	+	--	+	+
02→10	34→58	185	3.3	1.15	0	+	0	-	-	+	+
03→11	34→58	75	10	1.15	+	+	+	-	--	+	+
04→12	34→58	185	10	1.15	0	+	0	-	-	+	+
05→13	34→58	75	3.3	3	0	+	0	-	-	+	+
06→14	34→58	185	3.3	3	-	-	0	-	-	-	+
07→15	34→58	75	10	3	-	+	-	-	-	+	+
08→16	34→58	185	10	3	-	+	-	-	+	-	+
26→27	22→70	130	6.6	2.1	-	+	-	+	-	+	++

4.2.2.4 Conclusions on the Study of Elemental Release

The optimum leaching of carbonates, mainly those of magnesium and calcium, required low acid concentration and low temperature. These species seemed to dissolve fairly quickly (in the first half an hour) and simultaneously. Other minerals seemed to require a longer time for dissolution. A higher temperature was beneficial when the acid concentration was low. Also, when a stronger acid was used, a lower temperature

leaching was sufficient. Extraneous addition of ferric ions did not appear to play any important role.

This finding suggested a multistage treatment scheme, where carbonates are dissolved from coal in an early stage, lasting perhaps half an hour, in a relatively weak acid and at room temperature, followed by a second stage at room temperature with a stronger acid. This second stage will help removing the remaining magnesium. In the final stage of the processing, a long reaction time involving higher temperatures and low acid concentration will be necessary to remove the remaining species. Applying potentials at this point may improve the removal of the less soluble minerals, such as pyrite and silicates. A multistage test, using optimized conditions and a procedure derived from the previous conclusions was then executed.

4.2.3 Multistage Test Designed with the Best Operating Conditions - "BT"

The test was carried out with 100g of the same washed Jacob's Ranch coal (53-180 μ m). The H₂SO₄-HCl acid mixture (2-1 by volume of pure acid) was used. The five stages were organized as follows:

1. 1/2 hour in 750 ml of 1M acid (4.1%-2.1% by vol.) at room temperature;
2. 1/2 hour in 750 ml of 1M acid at room temperature;
3. 1 hour and 20 min. in 750 ml of 3M acid (12.5%-6.4% by vol.) at room temperature;
4. 1 hour and 40 min. in 750 ml of 1M acid at 60°C;

5. 2 hours and 30 min. in 750 ml of 1M acid at 60°C with 1 mM ferric ions, followed by water screening, resoaking in 1M sodium carbonate to extract sulfates remaining on coal, rinsing again, resoaking in 1M HCl and final rinsing.

The results of this experiment are reported in Table 40. The concentrations of the released main elements are reported in appendix B, and the graph in Figure 16 presents their concentration stage by stage.

Table 40. Effect of Multistage Procedure on Ash Removal from Washed Jacob's Ranch - Test "BT"

	Feed	St 1	St 2	St 3	St 4	St 5
Ash	7.0%	4.42%	3.77%	3.65%	3.38%	3.33%
Sulfur	0.58%	--	--	--	0.72%	0.75%
Ash Red	0	36.9%	46.1%	47.9%	51.7%	52.4%

The graph shows how significant were the dissolution of calcium, magnesium and iron carbonates in the two first stages. The next steps which lasted longer efficiently increased the ash removal and the elemental release. The third stage did not significantly improve the ash reduction, even after 80 minutes, and dissolution was poor. The fourth stage, involving higher temperature, was more efficient. Species like iron, calcium, aluminum and silica were still dissolving in the fifth stage, but much less than in the fourth. This fifth stage was actually useless, since little of the mineral matter remaining after 4 hours could be extracted, whatever the reaction time or the other conditions. Therefore, steps 3 and 5 should be eliminated to save energy, and stage 4 should be improved.

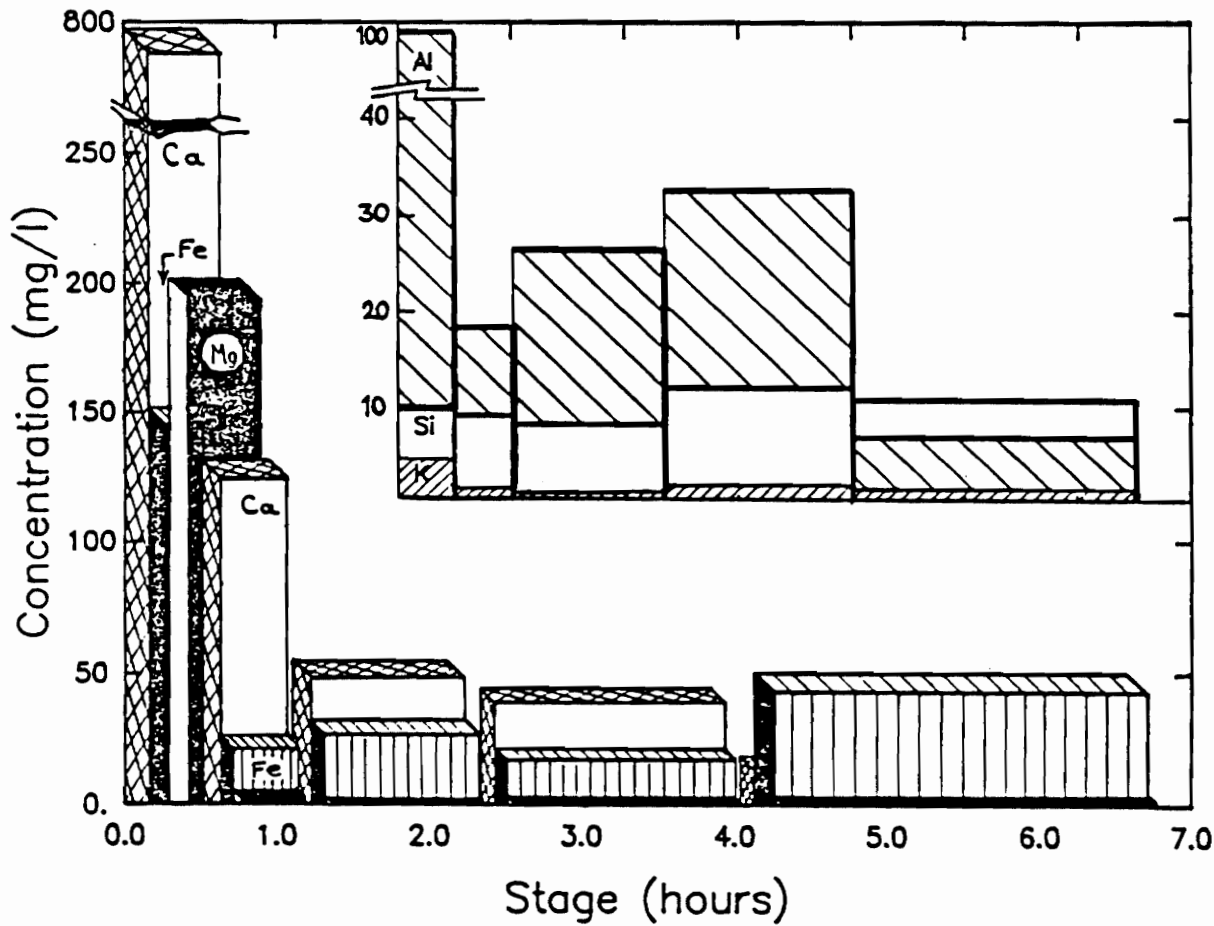


Figure 16. Elemental Concentrations in the Multistage Process of Jacob's Ranch (KMG)

5.0 ANALYSES and DISCUSSION

5.1 ANALYSES on PROPITIOUS COALS

Preceding studies revealed that some coals were better responding to the CECC than others. More detailed analyses on the feed, product, and leachates obtained from these coals were necessary to elucidate the mechanisms governing the process. This required:

- X-ray diffraction to identify the minerals present in the feed and in the product.
- Complete digestion of LT ash in acids to quantify the main compounds of the feed.
- Elemental analyses of the metals dissolved in the leachate.
- Mass balance to determine the extent of both liberation and dissolution in the whole mineral matter removal.
- SEM to study morphological changes associated with demineralization.

5.1.1 Analyses on Wyodak Coals

Most experiments conducted on Wyodak coals produced significant mineral matter removal. The sample chosen for x-ray diffraction, digestion, mass balance and SEM observations was the Jacob's Ranch from Kerr McGee (KMG), which was treated in the elutriation column. The other Jacob's Ranch delivered by North-Dakota University (NDU) was also used for mass balance calculations.

5.1.1.1 *X-ray Diffraction on the LT Ash*

The sample, 13g of wet-screened coal, was processed in 250ml of 3.2M acid mix (15.5%-13.5% H_2SO_4 -HCl by weight of pure acid) with EL (1v) for 6 hours and 30 minutes at 52°C. Recall the Jacob's Ranch KMG sample ash content was 10% for the run-of-mine, 6.35% for the washed feed coal, and 2.38% for the product coal.

LT Ash from Run-of-Mine Coal

The spectrum (see Figure 17) shows short but distinct peaks for quartz, a stronger peak for kaolinite and peaks for calcite mixed with dolomite, along with some bassanite interacting with siderite. Bassanite could be originated from calcite transformed during the LTA by recombination of sulfur with calcium. But the presence of bassanite was not doubtful since some was also observed with the SEM on the feed coal.

LT Ash from Wet-screened Feed Coal

Illite and kaolinite peaks appeared to be the same as before, but the quartz peak was obviously reduced; this indicated that a mere washing could reduce fair amount of

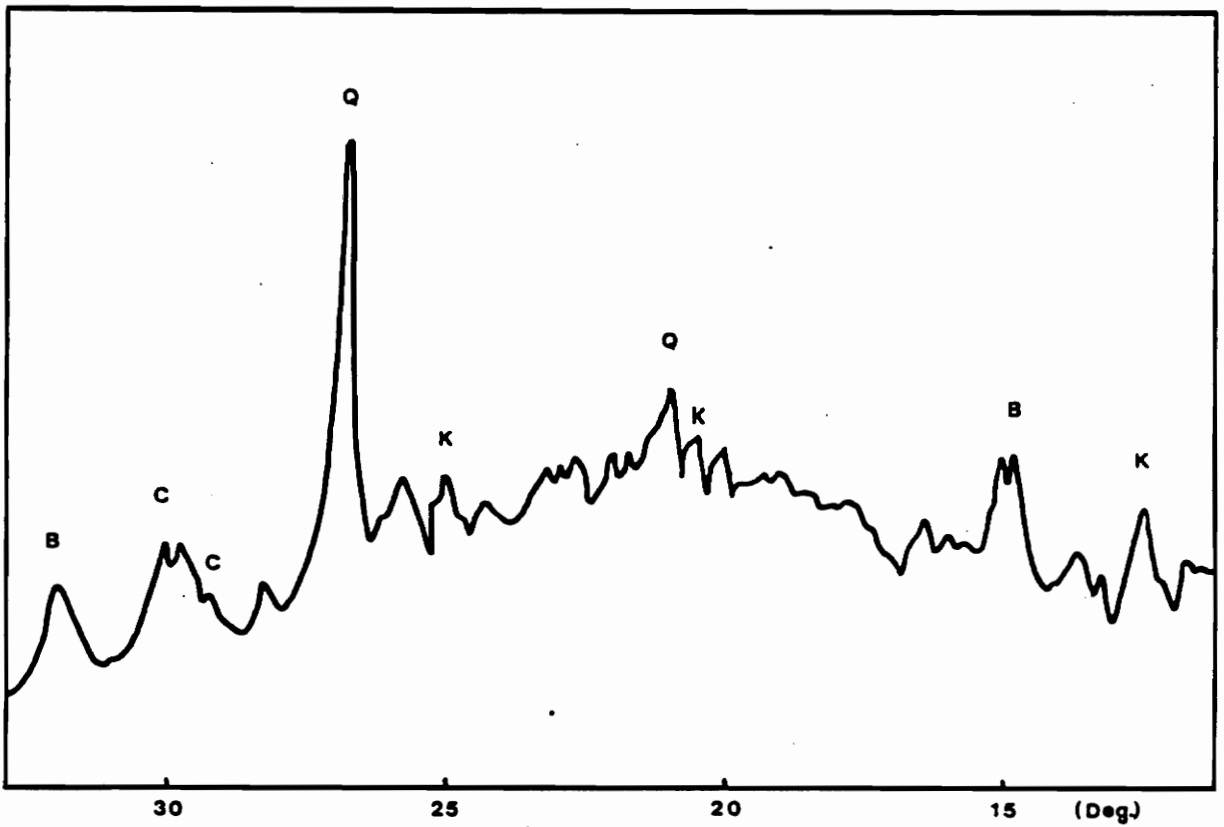


Figure 17. X-ray Diffraction Spectrum of Jacob's Ranch RoM Coal LT Ash: B = Bassanite; C = Carbonates; I = Illite; K = Kaolinite; Q = Quartz

the quartz held by simple adhesion on coal surface. The spectrum is shown in Figure 18. This finding suggests that quartz constitutes the majority of the slime coating.

LT Ash from Product Coal

As compared with the spectrum of the wet-screened feed, the product ash shows that the intensity of the ratio quartz over kaolin was increased, suggesting that the latter is preferentially removed during the CECC process. Note also that the bassanite peak is much weaker and that carbonate peaks are hardly discernable. These findings suggest that most of the soluble sulfates and carbonates were removed, which was in accordance with the results of the elemental analysis of the leachate. The spectrum is shown on Figure 19.

5.1.1.2 Acid Digestion of LT Ash

In order to quantify the different mineral compounds present in Jacob's Ranch KMG feed coal, the feed LT ash was digested according to the procedure already described (see chapter 3). The weight of LT ash was initially 15.3mg; the digestion was carried out in a mixture of HCl-HNO₃ (1:1 in volume) to dissolve all soluble minerals, and then in hydrochloric acid to solubilize silicates. After digestion, the weight of the dried residue was 1mg, which may represent unburned coal. The acid containing the dissolved matter was 83ml in volume. Table 41 lists the elemental concentrations and the corresponding proportions of compounds (refer to appendix C to convert elements into minerals).

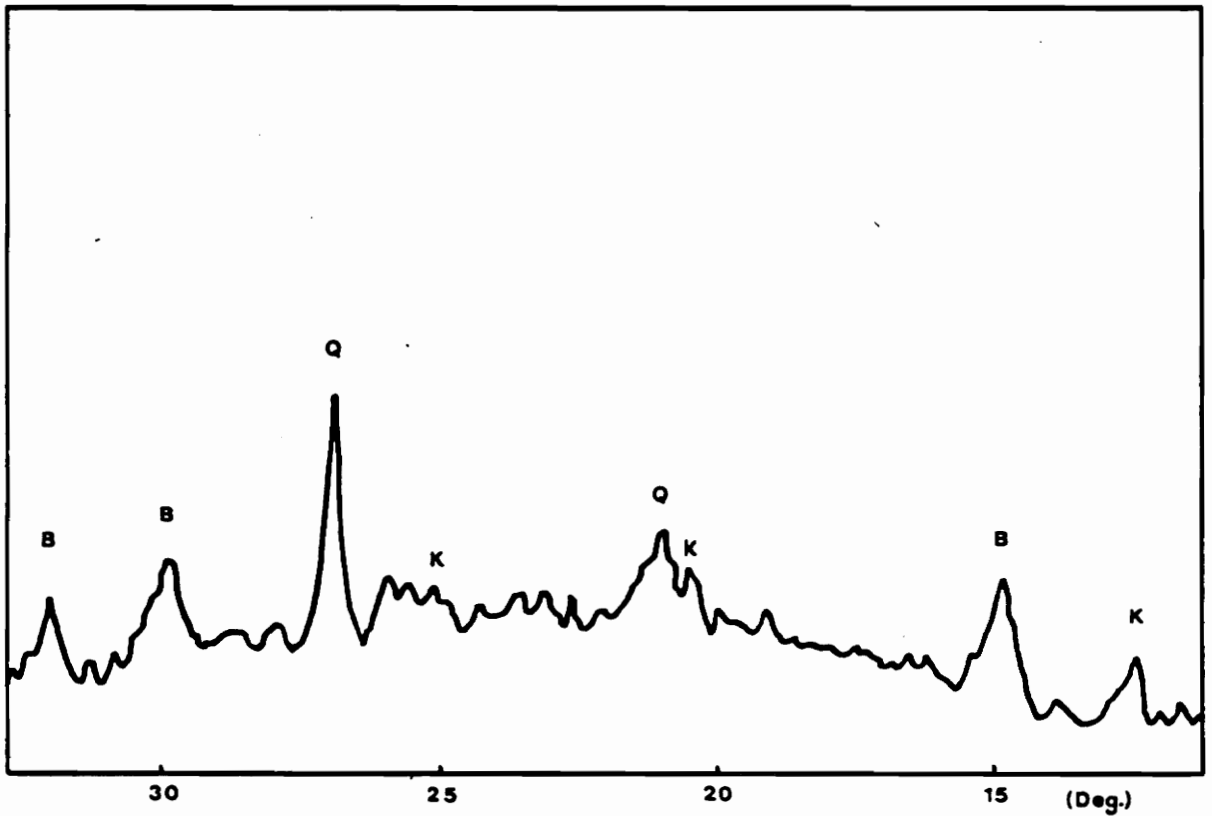


Figure 18. X-ray Diffraction Spectrum of Jacob's Ranch Wet-screened Feed Coal LT Ash: B = Bassanite; C = Carbonates; I = Illite; K = Kaolinite; Q = Quartz

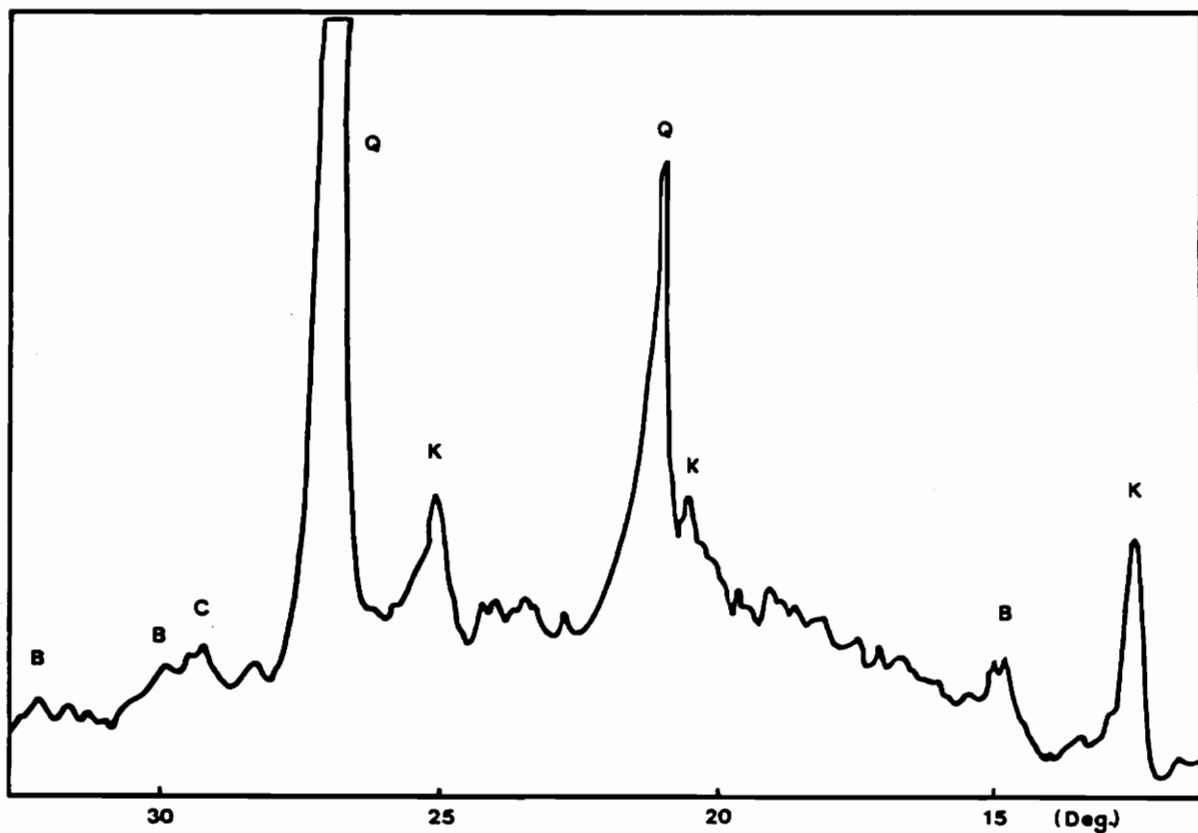


Figure 19. X-ray Diffraction Spectrum of Jacob's Ranch Column Product Coal LT
 Ash: B = Bassanite; C = Carbonates; I = Illite; K = Kaolinite; Q = Quartz

Table 41. Mass Balance of Low Temperature Ash Digested in Concentrated Acid, for Wet-screened Jacob's Ranch (KMG)

Elmt	Concentr. (mg/l)	Element Mass (mg)	Mineral Compound	Mineral Mass (mg)	Mineral Weight %
K	--	--	Illite	--	--
Al	5.276	0.4379	Kaolinite	2.127	14.9%
Si	5.82	0.4831	Quartz	0.058	0.4%
Mg	2.424	0.201	Dolomite	1.527	10.7%
Ca	16.45	1.365	Calcite	1.290	9.0%
			Bassanite	1.871	13.1%
Fe	10.46	0.868	Siderite	1.801	12.6%
Sum of Dissolved Compounds :				8.67 mg	
Mass of LT Ash Digested :				14.3 mg	
Percent Dissolution Reported :				60.7%	

Only 8.67mg of the mineral matter digested could be accounted for from the solution analysis. This represented only 60.7% of the total mass digested. The unaccounted 39.3% may be due to other minor minerals such as illite, pyrite and others.

5.1.1.3 Terms Used in Mass Balance Calculations

Some tests presented in this section have already been described in chapter 4, while some additional tests were especially designed to carry out the mass balance calculations.

In this section, results are given in terms of mineral matter weight and percent. Since some minerals are volatilized or dehydrated during the ashing procedure (750°C), ash weight is not exactly equivalent to mineral matter weight. Therefore, conversion from ash into mineral matter is necessary, and the Parr Formula (reformulated by the ASTM), is usually used:

$$\%MM = 1.1 \times \%Ash + 0.1 \times \%Sulfur \quad [1]$$

$$\text{or } \%Ash = 0.91 \times \%MM - 0.091 \times \%Sulfur \quad [2] \quad (\text{McClung and Geer, 1979}).$$

Percent sulfur was not always known in both feed and product, even though no dramatic difference was noticed between feed and product sulfur contents. Formula [1] was then used neglecting the term with sulfur :

$$\%MM = 1.1 \%Ash$$

In the case of a 5% ash and 1% sulfur coal, this simplification gives an error of only 2%, which may be acceptable.

Mass Balance Based on Solids

The mass balance based on solid content was calculated from the masses of ash in the feed, product and tail. From the masses of the feed, product and underflow and their respective ash contents, it was possible to calculate the mass balance of ash. The mass balance tables use the following terms:

- The *masses* of ash in the feed, product and underflow were termed by **Feed Ash**, **Prod Ash** and **Tail Ash**, respectively.
- The total mass of ash removed, **Ash Rem**, was equal to the mass of ash in the feed minus the mass of ash in the product.
- The mass of ash liberated was equal to the mass of ash in the underflow.

- The percent mineral matter liberated, **%MM Lib**, was equal to the mass of ash liberated over the mass of ash in the feed.
- The mass of ash dissolved, **Ash Diss**, was equal to the mass of ash removed minus the mass of ash liberated.
- The percent of mineral matter dissolved, **%MM Diss**, was equal to the mass of ash dissolved over the mass of ash in the feed.

Mass Balance Based on Leachate

The mass balance based on leachates are reported in a 5 column table. Each table has been set-up as follows: the first column lists the elements analyzed; the elemental concentrations are reported in the second column, and the mass of each element in the leachate in the third column; the fourth column lists the minerals containing the major element; the fifth column presents the mass of the mineral as calculated by multiplying the ratio of the mineral formula weight to the molecular weight of the element to the mass of the major element in solution (appendix C). From the data given in the table, the following information can be obtained:

- The **Total Mineral Matter Dissolved**, which is equal to the sum of the masses of all the dissolved compounds.
- The **Total Mineral Matter Removed**, which can be obtained from the mass balance on solids.
- The **Percent Dissolved**, which is the weight percent of the mineral matter present in the feed that dissolves.

- The **Percent Liberated**, which is equal to the complement to 100% of the percent dissolved.

5.1.1.4 Elemental Analysis on the Leachate from Jacob's Ranch LT Ash

A small sample of feed LT ash from the wet-screened Jacob's Ranch coal was submitted to simple leaching in conditions approaching those applied for a regular CECC test. This test on LT ash was to determine the maximum amount of mineral matter that can be dissolved from the feed. Since the coal matrix was burned away, all mineral matter was accessible to dissolution. This would allow one to determine the major compounds dissolved.

Procedure

A 40mg sample of LT ash (from 0.6g of feed coal) was mixed in a graduated cylinder with 6 ml of the 2.46M acid blend, a 10%-5.2% H₂SO₄-HCl mixture by volume of pure acid. The cylinder was held in a flask filled with water and heated at 65°C on a hot plate. After 7 hours and 10 min. of treatment with intermittent shaking, the content of the tube was filtered; the leachate was sent for elemental analysis, while the residue was rinsed, dried and weighed.

Mass Balance Based on Solids

The residue from the product after drying weighed 11.3mg. The balance, 28.7mg, had thus been dissolved, which represented 71.75% of the mineral matter originally contained in the feed. It is interesting to note that the very best regular tests conducted on Jacob's Ranch coal proved no more than 70% of ash removal, with the likelihood that some of the mineral matter was not accessible to the acid, thus to dissolution. This

leads to assume that, in the test with coal, the ash removal could not be ascribed to dissolution only, but, in some extent, to liberation.

Mass Balance Based on Leachate Analysis

The details of the mass balance based on elemental analysis are given in Table 42. This method shows that only 49.6% of the 40mg feed was dissolved, while the mass balance based on solid weight yielded 71.7%. The differences may be accounted for by the mass of other minor mineral matter that dissolved but were not taken into account by the elemental analysis. This discrepancy shows the limitation of the theoretical mass balance calculations based upon the analysis of leachate.

Table 42. Mass Balance Information Based on Elemental Analysis of Species from the Jacob’s Ranch (KMG), LT Ash of Wet-screened Feed

Elmt	Elemental Conc (mg/l)	Elemental Mass (mg)	Mineral	Mineral Mass (mg)
K	14.5	0.087	Illite	1.291
Al	163.4	0.980	Kaolinite	3.886
Si	67.75	0.407	Quartz	--
Mg	129.2	0.775	Dolomite	1.278
Ca	840.0	5.040	Calcite	4.696
			Bassanite	6.811
Fe	145.4	0.872	Siderite	1.880
Total Mass Dissolved :				19.842mg
Percent Dissolved :				49.6%

5.1.1.5 Mass Balance for Regular Tests Using Elemental Analysis and Balance on Solids

Mass Balance Based on Leachate for Jacob's Ranch (NDU)

Conditions: 25.2g of feed coal (75-210µm) assaying 8.9% ash was submitted to EL (1v) in 0.5M H₂SO₄ at 60°C for 8 hours and 15 minutes with ferric ions; 22.3g of product coal at 3.88% ash was collected. Table 43 reports the details of the mass balance.

Table 43. Proportion of Mineral Matter Dissolved by EL of the Wet-screened Jacob's Ranch (NDU) from the Balance on Leachate

Elmt	Elemental Conc (mg/l)	Elemental Mass (mg)	Mineral	Mineral Mass (mg)
K	10.5	7.87	Illite	116.9
Al	91.0	68.25	Kaolinite	252.4
Si	22.8	17.1	Quartz	--
Mg	75.2	56.4	Dolomite	428.0
Ca	235	176	Calcite	103.9
			Bassanite	150.7
Fe	244	Minimal	Siderite	45
Total MM Dissolved :				1097mg
Total MM Removed :				1521mg
Percent Dissolved :				72.1%
Percent Liberated :				27.9%

Based on mineral matter contents, and calculated from the ash contents using the Parr formula, the total mineral matter removed was found to be equal to 1521mg. According to this calculation, at least 72% of the removed mineral matter was dissolved. Results are consistent with the case of LT ash leaching (71.7%), which suggests that most of the mineral matter removed was due to dissolution. It is interesting to note, however, that the proportion of silicates dissolved in the present case is higher, which is difficult to explain.

Mass Balance Based on Solids for Jacob’s Ranch (NDU)

Conditions: 20g and 22g of feed coal (62-210µm) at 6.2% ash were subjected to SL and EL, respectively, in the H₂SO₄-HCl mixture (15.5%-13.5% by weight) at 56°C for 17 hours; 17.5g (for SL) and 19.55g (for EL) of product assaying 2.16% and 2.06% ash, respectively, were collected, along with 1.160g and 1.383g of underflow at 6.08% and 5.18% ash, respectively. Results for the mass balance on solids only are given in Table 44.

Table 44. Proportion of Mineral Matter Dissolved by SL and EL of the Wet-screened Jacob’s Ranch KMG from the Balance on Solids

Test	Feed Ash	Prod Ash	Tail Ash	Ash Rem	Ash Diss	%MM Diss	%MM Lib
SL	1.385g	0.403g	0.072g	0.952g	0.783g	91.7%	8.3%
EL	1.232g	0.378g	0.071g	0.854g	0.757g	91.3%	8.7%

The proportion of mineral matter removed by dissolution was over 90% in both cases of SL and E.L. Such a high ratio could be due to the prolonged time of treatment that might be responsible for the dissolution of liberated species.

Mass Balance for Jacob’s Ranch (KMG) After 1/2 hr SL (Test T)

All previous tests lasted several hours. It was of interest to calculate the mass balance and to quantify dissolution and liberation after a short processing time (half an hour). In this case, the dissolution of liberated minerals would be minimized and the data on dissolution more accurate. The test utilized was the statistical test “T” (refer to chapter 4, and to appendix B for the elemental analysis).

Conditions: 138g of feed coal (53-180µm) at 7.0% ash was treated by SL in 2.6M H₂SO₄-HCl mixture (10.6%-5.5% by volume) at 58.4°C for 1/2 hour, with addition of 11.3mM of ferric ions (0.631 mg/l); 135g of product at 3.80% ash were collected along with 4g of underflow at 5.0% ash. Results for the mass balance on solids are given in Table 45, and those on leachate are given in Table 46.

Table 45. Proportion of Mineral Matter Dissolved by 1/2 hour SL of Wet-screened Jacob’s Ranch (KMG) from the Balance on Solids

Feed Ash	Prod Ash	Tail Ash	Ash Rem	Ash Diss	%MM Diss	%MM Lib
9.722g	5.016g	0.200g	4.706g	4.506g	95.8%	4.2%

The mass balance based on elemental analysis indicated less dissolution. This may be due to the presence of various minor mineral matter, such as sphalerite, ankerite, halite, which have not been analyzed. Possible precipitation of calcium might have falsified the amount of calcite dissolved (only 148mg).

Table 46. Proportion of Mineral Matter Dissolved by 1/2 hour SL of Wet-screened Jacob's Ranch (KMG) from the Balance on Leachate

Elmt	Elemental Conc (mg/l)	Elemental Mass (mg)	Mineral	Mineral Mass (mg)
K	6.64	3.33	Illite	49.3
Al	293.0	146.5	Kaolinite	678.3
Si	9.86	4.93	Quartz	--
Mg	318.5	159.2	Dolomite	1208.4
Ca	763.0	381.5	Calcite	148.4
			Bassanite	215.2
Fe	707.6	353.8	Siderite	79.3
Total MM Dissolved :				2379mg
Total MM Removed :				5177mg
Percent Dissolved :				45.9%
Percent Liberated :				54.1%

After 4 hours of reaction, 53.3% of the ash was removed. Since 48.4% ash reduction was achieved after 1/2 hour, this meant that 90.8% of the mineral matter was removed within the first half an hour.

Figure 20 shows the release of the elements as a function of time. Calcium, highly released within the first half an hour, then dramatically decreased (by almost 50%), which is interpreted as precipitation. Meanwhile, aluminum, iron and magnesium did not increase much after the first hour of processing. Silica and potassium remained al-

most stationary after the first 1/2 hour. This graph supports the above observation by showing that most species had solubilized after a short period of time.

Mass Balance for Jacob's Ranch (KMG) After 1/2 hr SL at 25°C (Test BT)

The analyses presented here refer to the first stage of the multistage experiment designed for the optimum chemical cleaning. It differed from the previous one in that low temperature was employed, and no ferric ions were added. The mass balance on leachate should be more accurate for less precipitation was expected. The mass balance calculations were made on the basis of both solids and leachates.

Conditions: 100g of feed coal (53-180µm) at 7.0% ash was treated with SL in 1M H₂SO₄-HCl (4.1%-2.1% by volume) at room temperature for 1/2 hour; 92.4% of the feed was recovered in a product assaying 4.416% ash, along with 3.11g of underflow at 5.92%. Results for the mass balance on solids are given in Table 47, and those on leachate in Table 48.

Table 47. Proportion of Mineral Matter Dissolved by 1/2 hr of SL at 25°C of Jacob's Ranch (KMG) from the Balance on Solids

Feed Ash	Prod Ash	Tail Ash	Ash Rem	Ash Diss	%MM Diss	%MM Lib
7.0g	4.08g	0.184g	2.92g	2.736g	93.7%	6.3%

The correlation between both methods was better, for 87.4% versus 93.7% of the mineral matter was found to have dissolved. The balance, that is about 10%, could be considered as liberated.

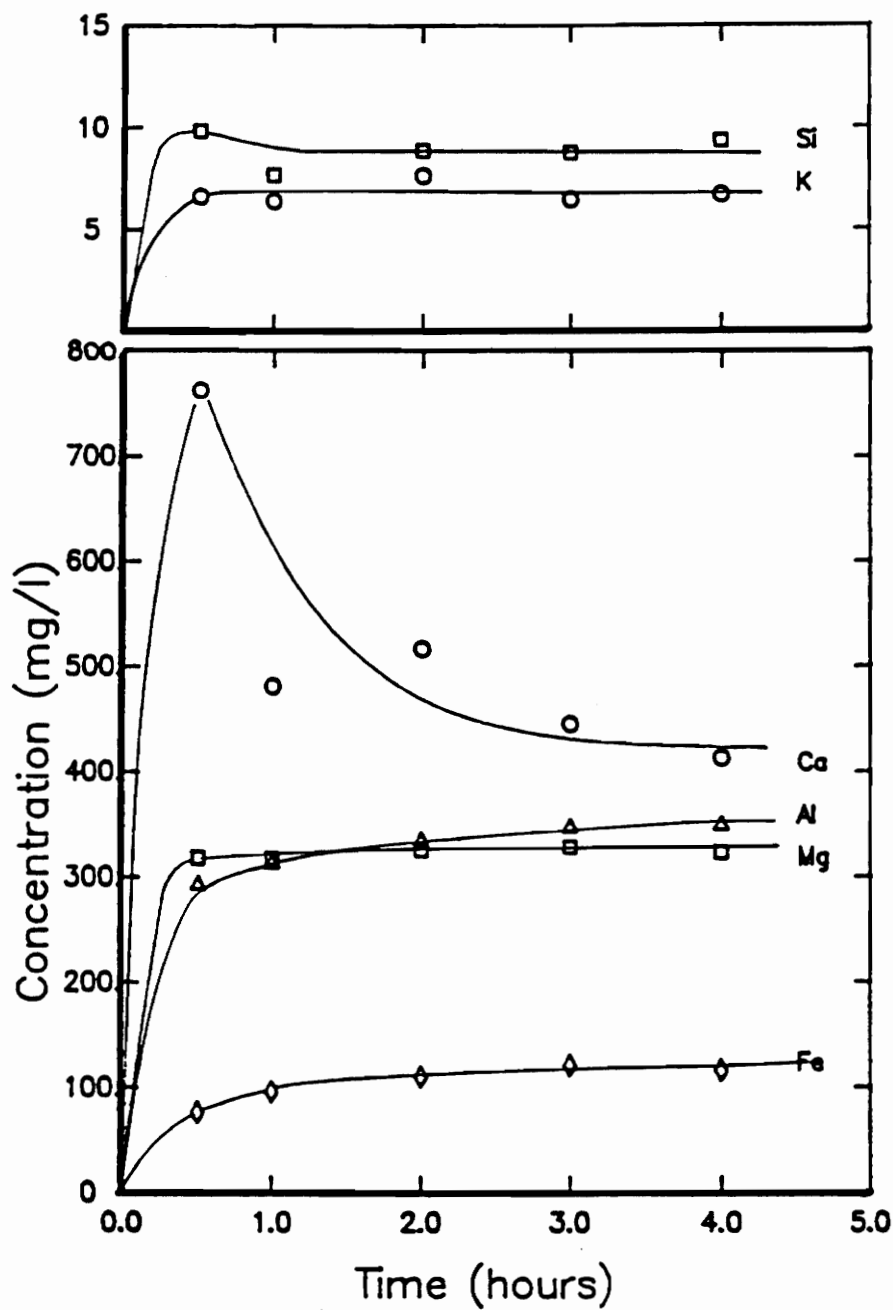


Figure 20. Elements Dissolved by SL of Washed Jacob's Ranch (KMG) - Test T

Table 48. Proportion of Mineral Matter Dissolved by 1/2 hour SL at 25°C of Jacob's Ranch (KMG) from the Balance on Leachate

Elmt	Elemental Conc (mg/l)	Elemental Mass (mg)	Mineral	Mineral Mass (mg)
K	4.47	3.35	Illite	49.7
Al	104.1	78.1	Kaolinite	345.6
Si	9.87	7.40	Quartz	--
Mg	201.8	151.4	Dolomite	1148.4
Ca	779.6	584.7	Calcite	418.3
			Bassanite	606.7
Fe	152.6	114.5	Siderite	237.4
Total MM Dissolved :				2806mg
Total MM Removed :				3212mg
Percent Dissolved :				87.4%
Percent Liberated :				12.6%

5.1.1.6 Scanning Electron Microscopy on Jacob's Ranch

The solids observed under the SEM were the particles from the feed and product of the Jacob's Ranch coal treated in the elutriation column. A 13g wet-screened coal sample was processed for 6 hours and 30 minutes at 52°C in 250ml of a 3.2M acid mix (15.5%-13.5% by weight of H₂SO₄-HCl) with EL (1v).

Run-of-Mine Coal

This coal appeared to be mostly composed of fusinite macerals, with characteristic tubular pores, 10-15 μ m in diameter, and a banded surface. The stripes seemed to be filled with silicates surrounded by packed carbonate grains. Numerous very small minerals (5 μ m), identified as calcite, siderite and illite, were found adhering to the maceral surface (see picture 1 on Figure 21).

Washed Feed Coal

The surface was almost devoid of any small adhering mineral. This proved the efficiency of wet-screening the coal before the CECC process. The pore structure appeared more clearly on picture 2 in Figure 21; the packed carbonates (1 μ m grains) filling up the pores, which also contained many clay plates, could easily be seen and characterized in the pore openings. The electron micrograph 3 in Figure 22 shows how siderite, much more common than pyrite, is incrustated in fusinite.

Washed Feed LT Ash

The whole structure was still better revealed by the LT ash. Quartz and kaolinite still mixed with unburned coal formed lenses of minerals; most abundant minerals were calcite, dolomite and bassanite, also found in bands. Electron micrograph 4 in Figure 22 exhibits the tremendous network of pore filling fine minerals mixed with clay plates.

Product Coal

Picture 5 on Figure 23 is a good example of a processed particle. The bands on the surface are more or less devoid of lens-shaped materials. Picture 6 shows the openings of the cavities clear of the soluble species, but not clear of the clays plates.

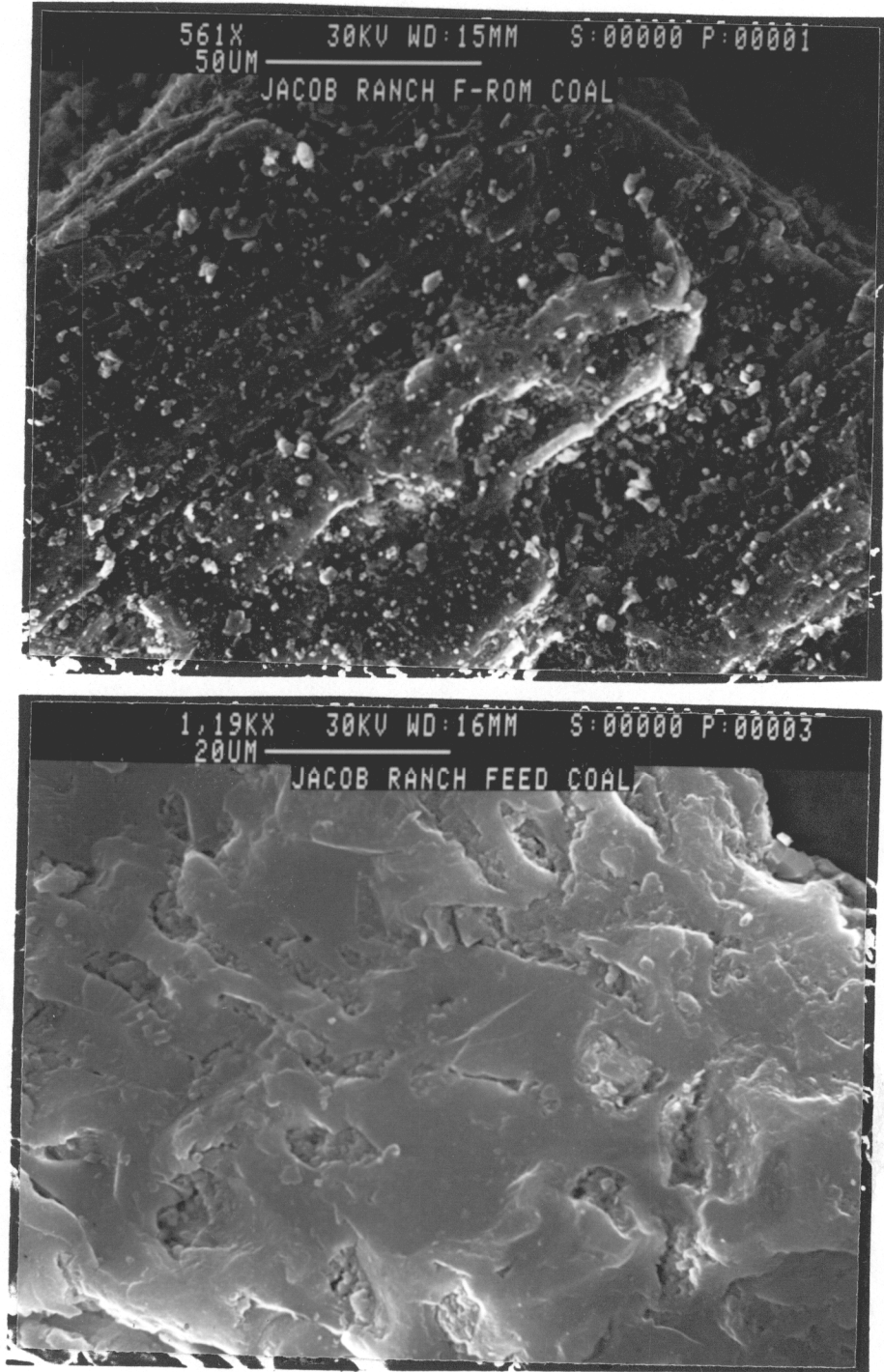


Figure 21. Electron Micrographs of Jacob's Ranch Wyodak Feed Coal: Above: 1 Run-of-mine Coal - Below: 2 Pores of Wet-screened Coal Filled with Clays and Carbonates

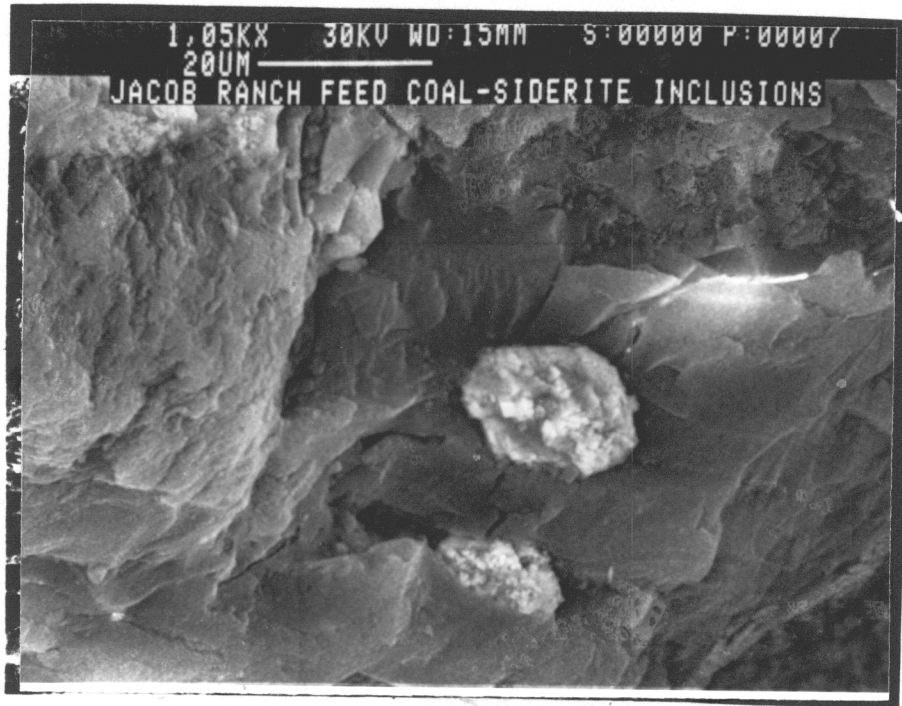


Figure 22. Electron Micrographs of Jacob's Ranch Wet-Screened Feed Coal: *Above:* 3 Siderite Inclusion - *Below:* 4 LT Ash Network (Fine Carbonates and Clay Lenses)

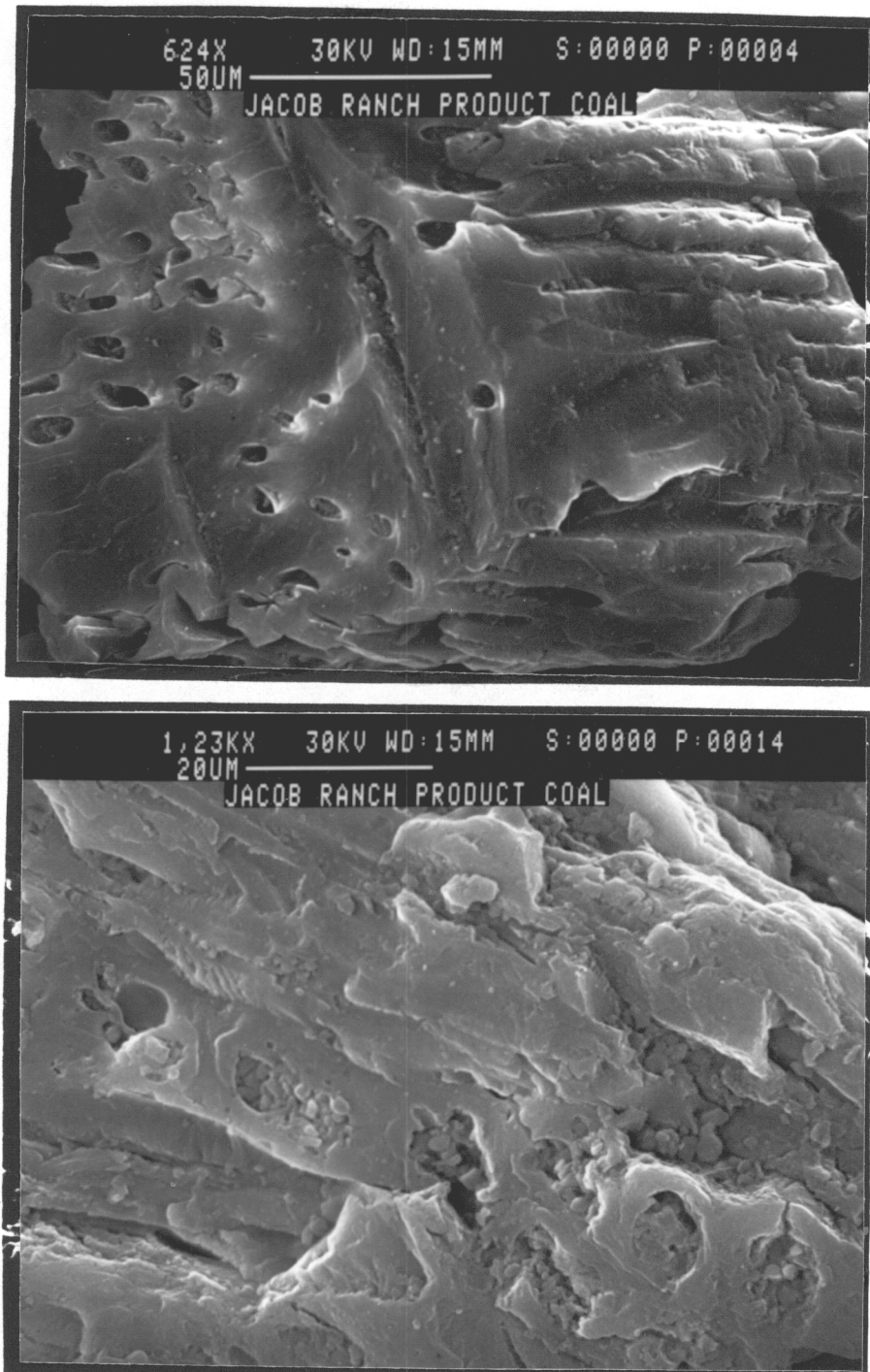


Figure 23. Electron Micrographs of Jacob's Ranch Product: *Above:* 5 Cleaned Fusinite -
Below: 6 Fusinite Pore Openings

Pictures 7 and 8 in Figure 24 show the surface of fusinite before and after the treatment. Picture 7 shows how clay lenses, sometimes mixed with coal, are held by tiny carbonates and sulfate bodies in the longitudinal pores. Picture 8 clearly shows that some of these lenses (about 50%) have been removed from their initial position on the surface. They may have been detached by dissolution of the soluble materials which had been holding them, but it is also possible that they were removed by osmotic pressure between the maceral and the lens. Most carbonates were gone, whereas sulfates partly remained, which could explain that sulfur is always high after processing.

Pictures 9 and 10 in Figure 25 show fusinite macerals before and after treatment. On picture 9, the longitudinal pores are amazingly filled with fine grains, identified as carbonates, enveloping clay plates, whereas on picture 10, they are rid of them, at least on the surface. Inclusions in the fusinite matrix, which appear as bright spots, are identified as mainly pyrite and quartz. All pyrite emerging from the maceral appear to be polished, probably under the action of leaching. Most of the time, a crack was present in the vicinity of the incrustated crystal, itself separated from the maceral walls by a narrow empty space; picture 11 in Figure 26 indicates that the inclusion, although surrounded by cracking, could not leave the matrix.

Product LT Ash

Quartz bodies were uneasy to locate in the LT ash, probably because of their small size, whereas typical packed plate-shaped clays were abundantly found, sometimes with unburned coal (see picture 12 in Figure 26). Bassanite was still present while carbonates had disappeared, confirming the previous statements. The small soluble minerals, so abundant in the initial feed LT ash, had totally disappeared. Therefore, carbonates, which were thought to be incompletely dissolved in the pores, had been actually leached out of the pores.

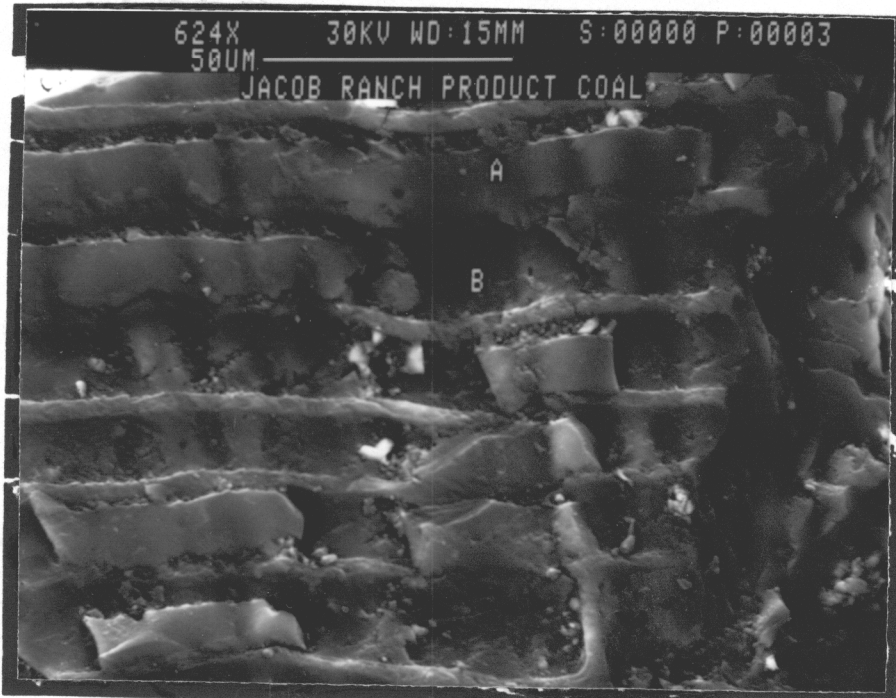
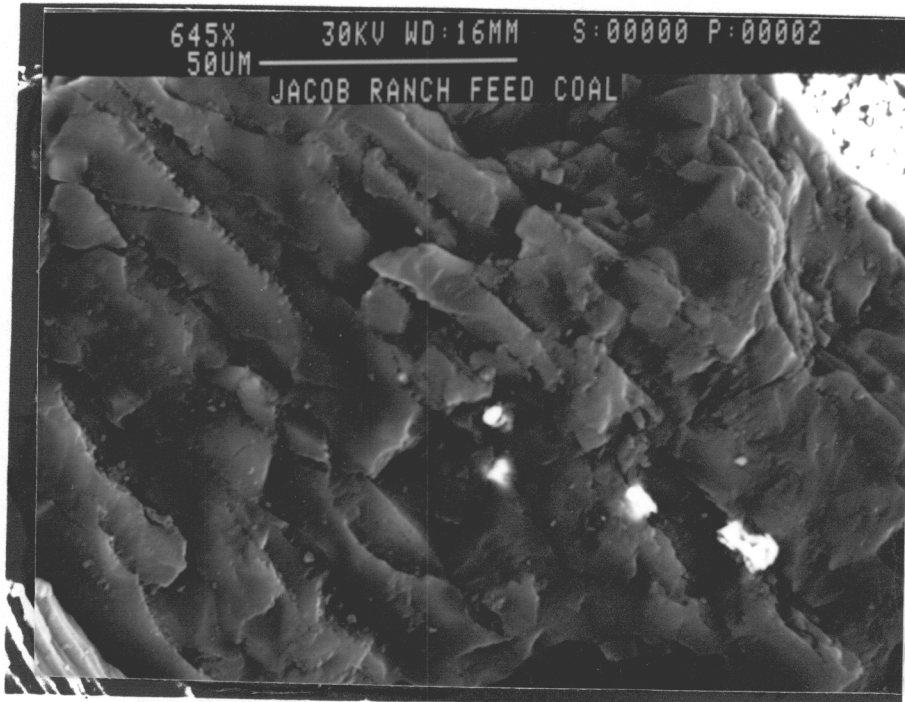


Figure 24. Electron Micrographs of Jacob's Ranch Before and After Treatment: Above: 7 Before Treatment - Below: 8 After Treatment

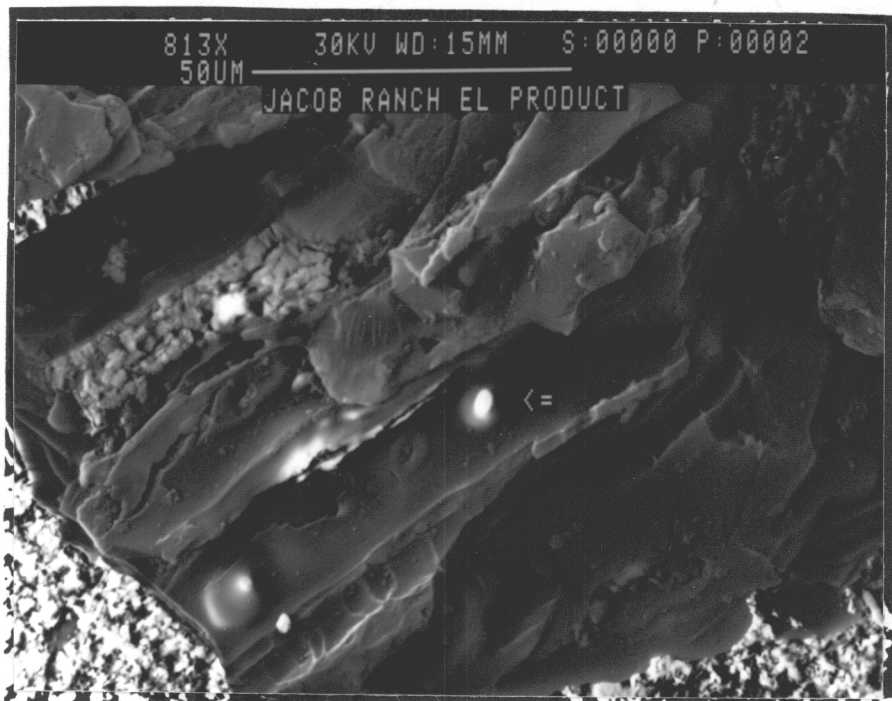
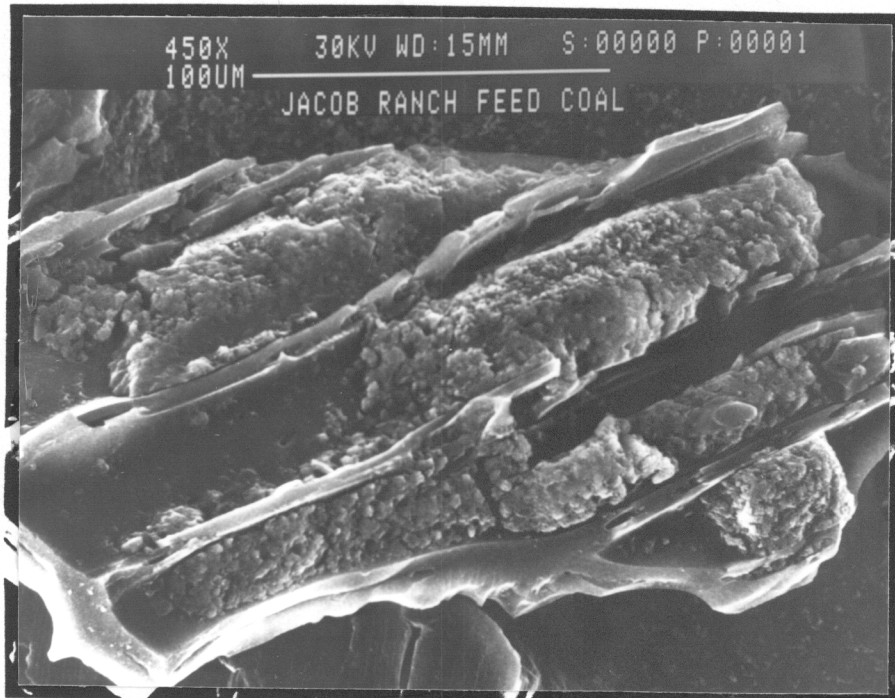


Figure 25. Electron Micrographs of Jacob's Ranch Pores: *Above:* 9 Before Treatment -
Below: 10 After Treatment

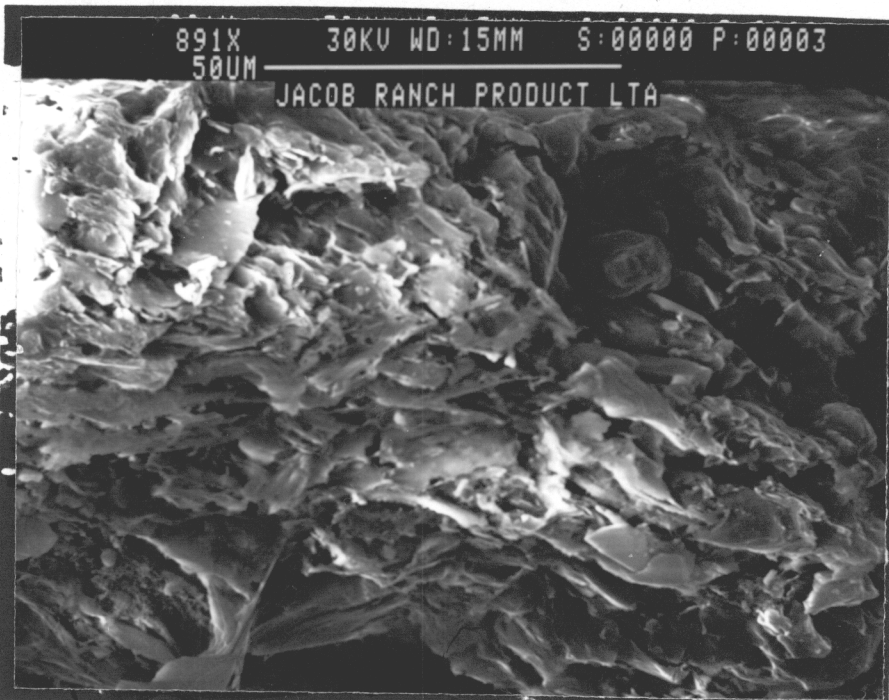


Figure 26. Electron Micrographs of Jacob's Ranch Product: *Above:* 11 Pyrite Inclusion -
Below: 12 Product LT Ash

5.1.2 Analyses on Widow Kennedy Coals

Widow Kennedy coals studied were very different from the Jacob's Ranch coals. First, macerals were mostly vitrinite versus fusinite for Jacob's Ranch. Also, these vitrinite macerals contained much more pyrite. Finally, a good mineral matter removal from Widow Kennedy coal required a long processing time, whereas most of minerals were removed from the Jacob's Ranch coal in one hour. X-ray diffraction and acid digestion tests were conducted on Widow Kennedy Dominion #1 samples, and elemental analysis, mass balance and SEM studies were conducted on both Widow Kennedy Wellmore and Dominion #1 coals.

5.1.2.1 X-ray Diffraction

LT ash samples, obtained from the test carried out in the stirred vessel, were subjected to x-ray analysis: 22.7g of floated coal (53-210 μ m) were treated in 500ml of 3.2M acid mixture (H₂SO₄-HCl, 15.5%-13.5% by weight) at 60°C for 10 hours and 40 minutes with 1v applied potential (EL). The run-of-mine coal assaying 43.5% ash, which was cleaned by flotation and a feed sample assaying 3.38% was obtained. The product assayed 1.66% ash after the CECC process.

LT Ash from Run-of-mine Coal

The x-ray spectrum shown in Figure 27 demonstrates the presence of illite, kaolinite, quartz, anhydrite and calcite. Small amounts of dolomite (or ankerite) and siderite were also detected.

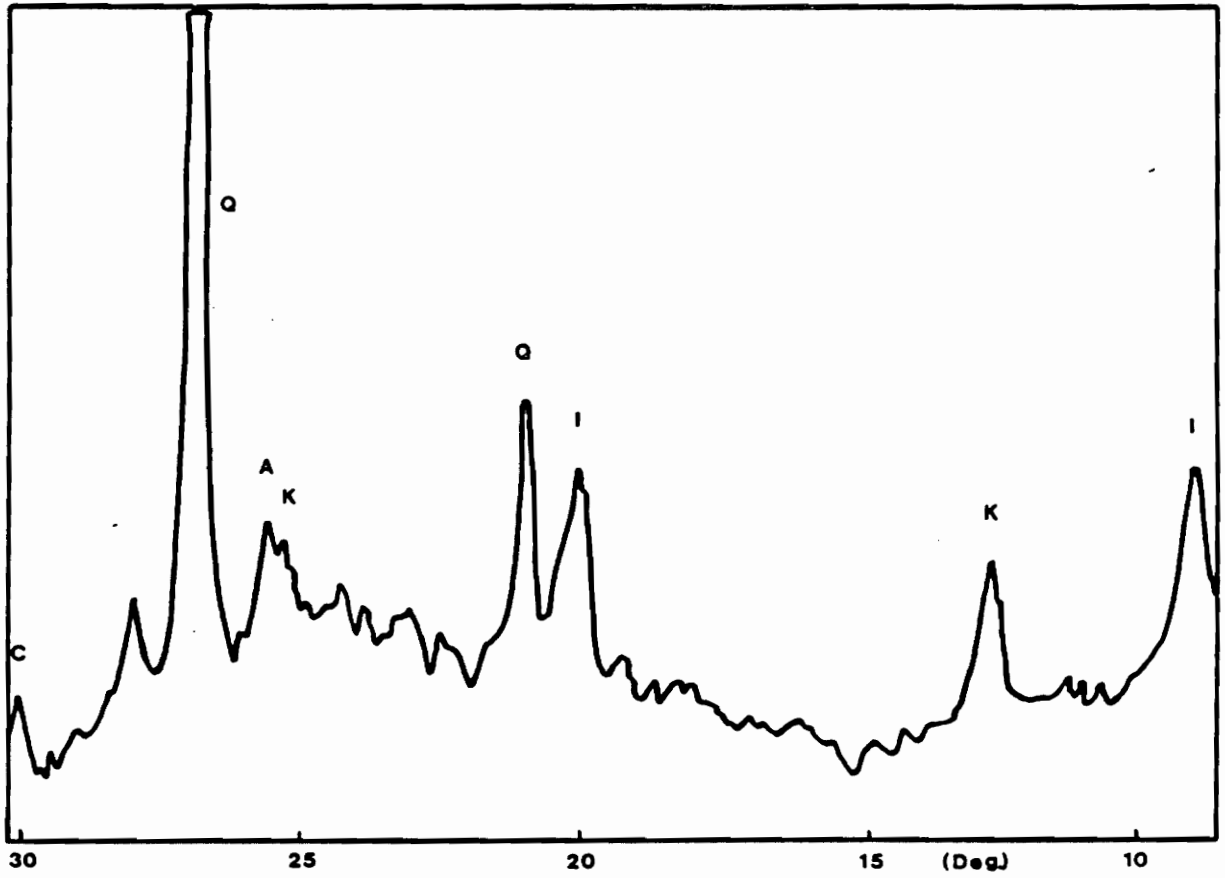


Figure 27. X-ray Diffraction Spectrum of Widow Kennedy Dominion #1 RoM LT Ash: A = Anhydrite; C = Carbonates; I = Illite; K = Kaolinite; Q = Quartz

LT Ash from Floated Feed Coal

Figure 28 shows that illite and quartz peaks were significantly reduced relative to kaolinite. The same tendency was observed for Jacob's Ranch, confirming again that the small bodies adhering to the surface are mostly quartz crystals and illite particles. This was probably because quartz and illite were rarely disseminated through the coal matrix, and were mostly found in the bedding planes of the coal seams. Therefore, these minerals may be readily broken during mining and then likely to adhere to larger particles of coal. Sulfate and carbonate minerals remained nearly unchanged after flotation.

LT Ash from Product Coal

The x-ray spectrum shows that illite, kaolinite and quartz were not much reduced. Anhydrite had decreased substantially and carbonates had decreased moderately (Figure 29).

5.1.2.2 Acid Digestion of LT Ash

A total of 143.1mg of LT ash was digested in hot concentrated HCL-HNO₃ mixture (please refer to the procedure in chapter 3). After digestion, the weight of the residue was 9.4mg, which included unburned coal, so that the digested mineral matter weight was 133.7mg. The acid matrix containing the dissolved elements was 83.5ml in volume. Table 49 lists the elemental concentrations and the masses and proportions of the mineral matter compounds. Detailed procedures are given in appendix C.

As much as 86.2% of the mass of LT ash digested could be back-calculated from the sum of the dissolved mineral matter compounds, thus, the mass balance seemed to be reasonably accurate. It is interesting to note that there was not enough calcium to

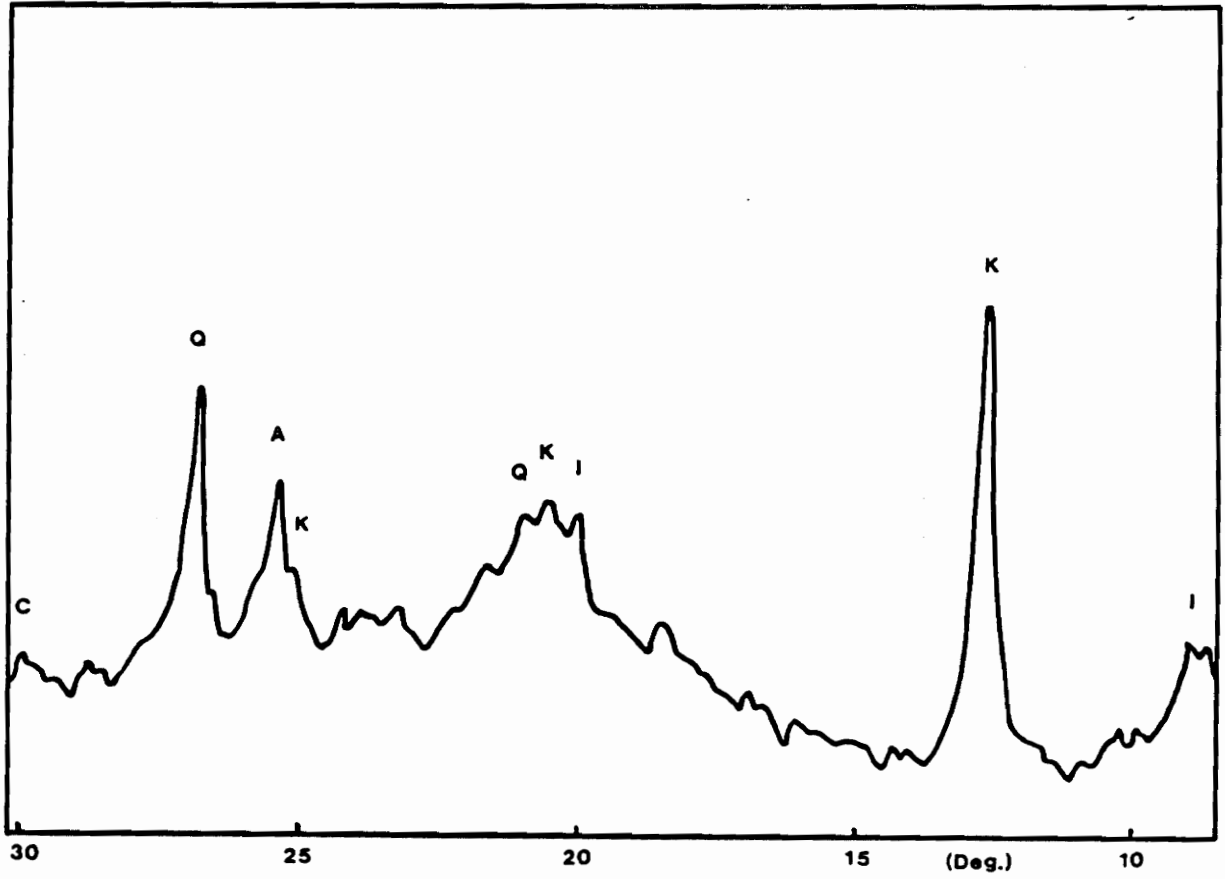


Figure 28. X-ray Diffraction Spectrum of Widow Kennedy Dominion #1 Floated Feed LT Ash: A = Anhydrite; C = Carbonates; I = Illite; K = Kaolinite; Q = Quartz

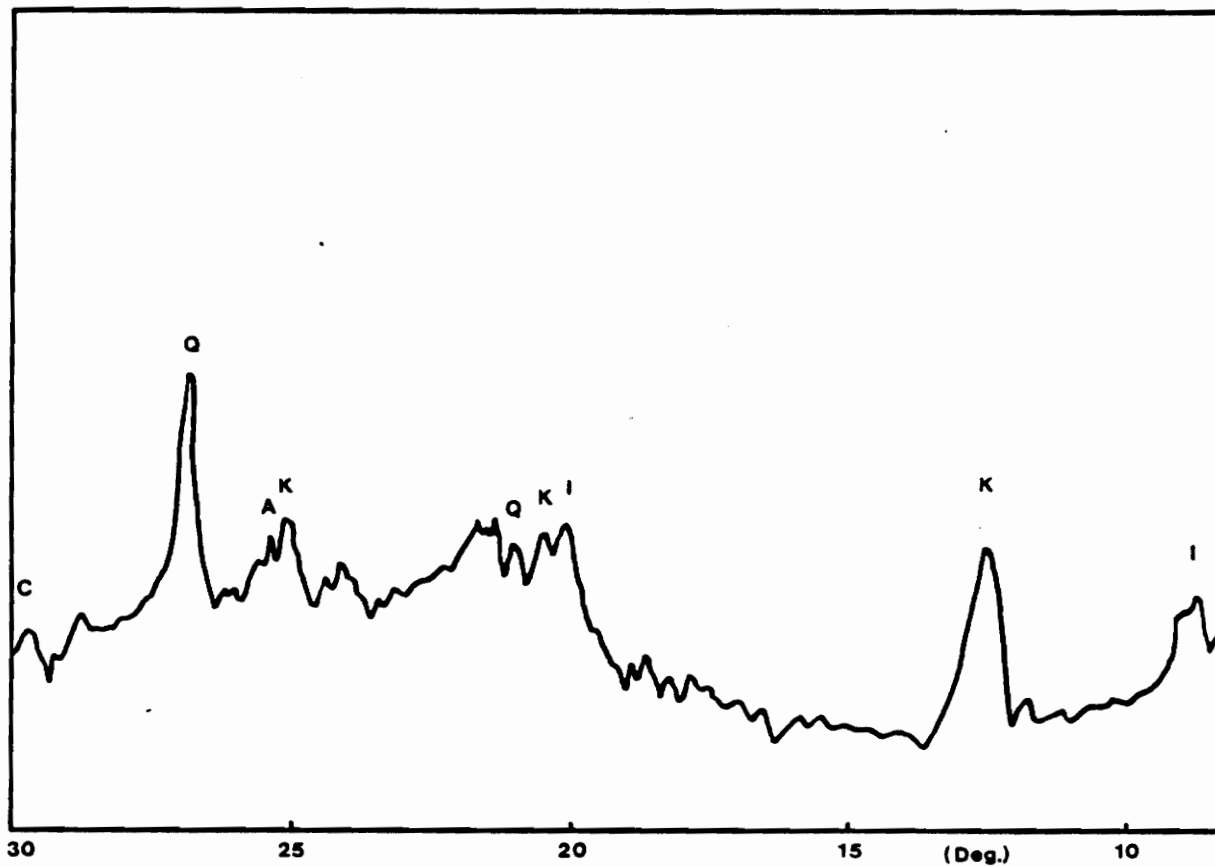


Figure 29. X-ray Diffraction Spectrum of Widow Kennedy Dominion #1 Product LT Ash: A = Anhydrite; C = Carbonates; I = Illite; K = Kaolinite; Q = Quartz

Table 49. Mass Balance of Low Temperature Ash Digested in Concentrated Acid, for Cleaned Widow Kennedy Dominion #1

Elmt	Concentr. (mg/l)	Element Mass (mg)	Mineral Compound	Mineral Mass (mg)	Mineral Weight %
K	--	--	Illite	--	--
Al	138.2	11.54	Kaolinite	56.1	41.9%
Si	386.9	32.31	Quartz	43.4	32.5%
Mg	4.24	0.35	Dolomite	2.69	2.0%
Ca	1.88	0.16	Calcite	--	--
			Bassanite	--	--
Fe	73.32	6.12	Pyrite	13.14	9.8%
Sum of Dissolved Compounds :					115.3 mg
Mass of LT Ash Digested :					133.7 mg
Percent Dissolution Reported :					86.2%

be converted into calcite after the calculation of dolomite weight from calcium (please refer to appendix C), although x-ray analyses proved the presence of calcite and bassanite. Furthermore, potassium was not analyzed, which made it impossible to calculate the amount of illite. Nevertheless, the predominance of silicates and the high proportion of pyrite (about 10%) in the mineral matter was confirmed.

5.1.2.3 Elemental Analysis on the Leachate from Widow Kennedy LT Ash

Like Jacob's Ranch coal, the LT ash of the feed coal was submitted to simple leaching to study the dissolution of minerals in absence of coal. The procedure was identical, using 0.0099g of floated Dominion #1 LT ash, equivalent to the mineral matter present in 0.296g of a feed coal assaying 3.38% ash. The LT ash was mixed with 1.5ml of the 2.46M acid (10%-5.2% H₂SO₄-HCl by volume of pure acid), and then processed at 60°C for 7 hours and 10 minutes. The results presented in Table 50 give the mass of compounds dissolved. Since the product residue could not be weighed, the mass balance on solids could not be calculated.

Iron was the most abundant element, which confirmed the high presence of pyrite in the flotation concentrate, although pyrite was not visible on the x-ray spectrum. The abundance of pyrite will be confirmed by the SEM study. Calcium was also abundantly released. This method indicated that 33% of the total mass dissolved was due to silicates.

5.1.2.4 Mass Balance for Regular Tests Using Elemental Analysis and Balance on Solids

Mass Balance for RoM Widow Kennedy Wellmore Coal

Conditions: 25g of run-of-mine coal (210-840µm) at 30.3% ash were subjected to the CECC process with 1v applied potential in 3.2M H₂SO₄-HCl mixture (15.5%-13.5% by weight) at 60°C for 8 hours; 20.90g of product assaying 21.75% ash were collected along with 3.151g of underflow that assayed 68.17% ash. Results for the mass balance on solids and on leachate are given in Table 51 and Table 52.

Table 50. Mass Balance Information Based on Elemental Analysis of Species from the Widow Kennedy Dominion #1, LT Ash of Cleaned Feed

Elmt	Elemental Conc (mg/l)	Elemental Mass (mg)	Mineral	Mineral Mass (mg)
K	29.95	0.045	Illite	0.668
Al	185.1	0.278	Kaolinite	0.898
Si	134.5	0.202	Quartz	--
Mg	42.83	0.064	Dolomite	0.486
Ca	247.6	0.371	Calcite	0.663
Fe	575.0	0.862	Pyrite	1.850
Total MM Dissolved :				4.565mg
Percent Dissolved :				46.1%
Percent Liberated :				None

Table 51. Proportion of Mineral Matter Dissolved by EL of Run-of-mine WK Wellmore from the Balance on Solids

Feed Ash	Prod Ash	Tail Ash	Ash Rem	Ash Diss	%MM Diss	%MM Lib
7.584g	4.546g	2.148g	3.038g	0.890g	29.3%	70.7%

In the case of using a RoM coal not initially wet-screened, a minimum of 45% and a maximum of 70% of mineral matter was found to be liberated. The discrepancy between the two methods of calculating the percent of liberation was significant, yet may

Table 52. Proportion of Mineral Matter Dissolved by EL of Run-of-mine WK Wellmore from the Balance on Leachate

Elmt	Elemental Conc (mg/l)	Elemental Mass (mg)	Mineral	Mineral Mass (mg)
K	20.8	15.6	Illite	231.5
Al	178.0	133.5	Kaolinite	491.7
Si	32.2	24.1	Quartz	--
Mg	60.8	45.6	Dolomite	346.0
Ca	241.0	180.7	Calcite	263.5
Fe	312.0	234.0	Pyrite	502.2
Total MM Dissolved :				1835mg
Total MM Removed :				3342mg
Percent Dissolved :				54.9%
Percent Liberated :				45.1%

be acceptable. These results show as expected that the removal of adhering particles from a run-of-mine coal could be misleadingly accounted as liberation, while most of them could have been removed by a mere washing.

First Mass Balance for Widow Kennedy Wellmore, Cleaned by Heavy Medium, Reground and Dry-sieved

This test was a 3-stage processing conducted on the Wellmore coal, cleaned by heavy-media separation (1 to 5mm). The heavy medium concentrate was reground to

obtain a proper size feed. After pulverization, the coal was dry-screened to obtain appropriate size fractions.

First Stage Conditions: 25g of a partly clean feed coal (62-210 μ m) at 8.2% ash was processed with 1v applied potential in 3.2M H₂SO₄-HCl acid (15.5%-13.5% by weight) at 60°C for 6 hours and 50 minutes. 24.17g of the product assaying 6.16% ash were collected along with 0.8g of underflow (29.72% ash). Results for the mass balance on solids and on leachate are given in Table 53 and in Table 54.

Table 53. Proportion of Mineral Matter Dissolved by EL of Cleaned and Reground WK Wellmore from the Balance on Solids

Feed Ash	Prod Ash	Tail Ash	Ash Rem	Ash Diss	%MM Diss	%MM Lib
2.047g	1.489g	0.238g	0.558g	0.320g	57.3%	42.7%

Depending on the method, between 57 and 75% of the removal of mineral matter in the first stage was found to be due to dissolution, which suggested that significant portion of the mineral matter was removed by liberation. Elemental analysis was also conducted on the leachate obtained without applied potential. The concentrations were fairly similar, except for calcium whose concentration was 210 mg/l; compared to the 37.7 mg/l obtained with applied potential which may be related to the reprecipitation problem noted for Jacob's Ranch coal.

Second Mass Balance for Widow Kennedy Wellmore, Cleaned by Heavy Medium, Reground and Wet-screened

Conditions: 122g of wet-screened feed coal (62-300 μ m) assaying 6.43% ash were processed with 1v applied potential in 3.2M H₂SO₄-HCl mixture (15.5%-13.5% by weight) at 62°C for 8 hours. The product (121.3g) assayed 5.09% ash, and the tail,

Table 54. Proportion of Mineral Matter Dissolved by EL of Cleaned and Reground WK Wellmore from the Balance on Leachate

Elmt	Elemental Conc (mg/l)	Elemental Mass (mg)	Mineral	Mineral Mass (mg)
K	10.5	7.87	Illite	116.9
Al	48.0	36.0	Kaolinite	95.7
Si	19.6	14.7	Quartz	--
Mg	14.7	11.0	Dolomite	83.7
Ca	37.7	28.3	Calcite	25.2
Fe	88.0	66.0	Pyrite	141.6
Total MM Dissolved :				463.1mg
Total MM Removed :				613.8mg
Percent Dissolved :				75.4%
Percent Liberated :				24.6%

weighing 0.45g, assayed 21.6% ash. The results of mass balance on solids are listed in Table 55 and those on leachate in Table 56.

Table 55. Proportion of Mineral Matter Dissolved by EL of Cleaned, Reground and Wet-screened WK Wellmore from the Balance on Solids

Feed Ash	Prod Ash	Tail Ash	Ash Rem	Ash Diss	%MM Diss	%MM Lib
7.716g	6.174g	0.097g	1.542g	1.445g	93.7%	6.3%

Table 56. Proportion of Mineral Matter Dissolved by EL of Cleaned, Reground and Wet-screened WK Wellmore from the Balance on Leachate

Elmt	Elemental Conc (mg/l)	Elemental Mass (mg)	Mineral	Mineral Mass (mg)
K	64.6	48.5	Illite	--
Al	95.6	71.7	Kaolinite	348.2
Si	--	--	Quartz	--
Mg	29.9	21.7	Dolomite	164.8
Ca	124.4	93.3	Calcite	143.4
Fe	281.6	211.2	Pyrite	455.3
Total MM Dissolved :				1112mg
Total MM Removed :				1696mg
Percent Dissolved :				65.6%
Percent Liberated :				34.4%

Aluminum was not found in a sufficient amount in the leachate for the conversion into both illite and kaolinite. It was decided to neglect illite and to calculate only the mass of kaolinite. Between 65.6% and 93.7% of the mineral matter removed were ascribed to dissolution, versus 57% in the previous section dealing with the same coal. It should be recalled that the present sample was wet-screened before the test, which removed free minerals, whereas the previous sample was only dry-screened after regrinding. The poor performance in sulfur removal (0.98% in the feed for 0.95% in the product) could be due to the short processing time.

Mass Balance for Wet-screened Widow Kennedy Winston #9 Electroleaching

Conditions: 85g of wet-screened coal (53-300 μ m) assaying 26.4% ash were first pre-soaked in 3.2M H₂SO₄-HCl acid (15.5%-13.5% by weight) for 10 hours at room temperature. The CECC process involving EL was then conducted in the same electrolyte at 57°C for 10 hours.

By washing the run-of-mine coal on the 53 μ m sieve, 20% of the sample weight (fines) was removed. The product, weighing 80.9g, was assaying 23.6% ash, and the tail, weighing 2.164g, was assaying 60% ash. Results of mass balance on solids are shown in Table 57 and results on leachate in Table 58.

Table 57. Proportion of Mineral Matter Dissolved by EL of Wet-screened WK Winston #9 from the Balance on Solids

Feed Ash	Prod Ash	Tail Ash	Ash Rem	Ash Diss	%MM Diss	%MM Lib
22.45g	19.11g	1.299g	3.34g	2.041g	61.1%	38.9%

The recovery amounted to 85.1%, but the ash reduction (10.6%) and the ash removal (14.9%) were too low for this coal to be considered as a candidate for CECC. Also, the mass balance indicated that even after long presoaking and processing, between 61% and 71% of the mineral matter removed was dissolved. The sulfur content slightly decreased from 1.44% to 1.33%, indicating removal of some pyrite.

Table 58. Proportion of Mineral Matter Dissolved by EL of Wet-screened WK Winston #9 from the Balance on Leachate

Elmt	Elemental Conc (mg/l)	Elemental Mass (mg)	Mineral	Mineral Mass (mg)
K	71.6	53.7	Illite	797.0
Al	194.6	145.9	Kaolinite	168.9
Si	29.7	22.3	Quartz	--
Mg	86.5	64.9	Dolomite	492.5
Ca	101.7	76.3	Calcite	--
Fe	541.0	405.7	Pyrite	1,161.0
Total MM Dissolved :				2619mg
Total MM Removed :				3674mg
Percent Dissolved :				71.3%
Percent Liberated :				28.7%

Mass Balance for Floated Widow Kennedy Dominion #1 in the Elutriated Column

Conditions: The run-of-mine feed coal (47.7% ash), was floated in stages, then wet-screened and processed in the column. Then, 30g of washed feed coal (62-210µm) assaying 3.45% ash were subjected to the CECC process with applied potentials in 2.46M H₂SO₄-HCl acid mixture (10%-5.2% by volume) with 9.59mM of ferric ions at 53°C for 7 hours and 10 minutes. The product, weighing 29g, assayed 2.43% ash, and the tail, weighing 0.69g, assayed 7.1% ash. The results of the mass balance on solids are shown in Table 59 and the results on leachate in Table 60.

Table 59. Proportion of Mineral Matter Dissolved by EL in Column of Cleaned WK Dominion #1 from the Balance on Solids

Feed Ash	Prod Ash	Tail Ash	Ash Rem	Ash Diss	%MM Diss	%MM Lib
1.035g	0.705g	0.049g	0.330g	0.281g	85.2%	14.8%

The mass balance calculations indicated that between 67.5% and 85% of the total removal of mineral matter was due to dissolution. The physically clean coal probably had less material available for liberation.

Figure 30 shows the kinetics of release of the main elements during the CECC process that lasted 17 hours. The release of Al, Mg and Fe reached a plateau after about 7 hours. The decrease in Ca concentration was probably due to reprecipitation.

The amount of ferric ions added being known, the release of iron could be determined by subtraction of the iron added from the total of iron species in solution. After ten hours, the iron release reached a plateau, as if pyrite was not oxidized anymore.

5.1.2.5 Scanning Electron Microscopy on Widow Kennedy Wellmore

The electron micrographs shown in this section were shot on Widow Kennedy Wellmore feed and product samples. The coal was first cleaned by heavy-media, re-ground and then processed in the multistage treatment with electrolysis. The feed contained 8.18% ash, the product assayed 6.16% ash after the first stage (6 hours and 50 minutes at 60°C, 25g of coal in 750ml of 15.5%-13.5% H₂SO₄-HCl mixture. The product of the second stage was assaying 3.89% ash (after 11 hours and 30 minutes at

Table 60. Proportion of Mineral Matter Dissolved by EL in Column of Cleaned WK Dominion #1 from the Balance on Leachate

Elmt	Elemental Conc (mg/l)	Elemental Mass (mg)	Mineral	Mineral Mass (mg)
K	2.73	2.73	Illite	4.5
Al	16.3	16.3	Kaolinite	51.9
Si	14.7	14.7	Quartz	--
Mg	4.9	4.9	Dolomite	37.2
Ca	43.5	43.5	Calcite	44.2
			Bassanite	64.1
Fe	401.9	401.9	Pyrite	7.3
Total MM Dissolved :				245.2mg
Total MM Removed :				363.0mg
Percent Dissolved :				67.5%
Percent Liberated :				32.5%

60°C, using 7g of the first stage product, in 600ml of the same mix diluted to 6.2%-2.1%).

Feed Coal

The feed coal was composed mainly of vitrinite with a few fusinite macerals. Vitrinite was mostly smooth and clean, but clay flakes were often found on the maceral surface (middlings). Calcite was also frequently found covering coal grains. Pyrite was

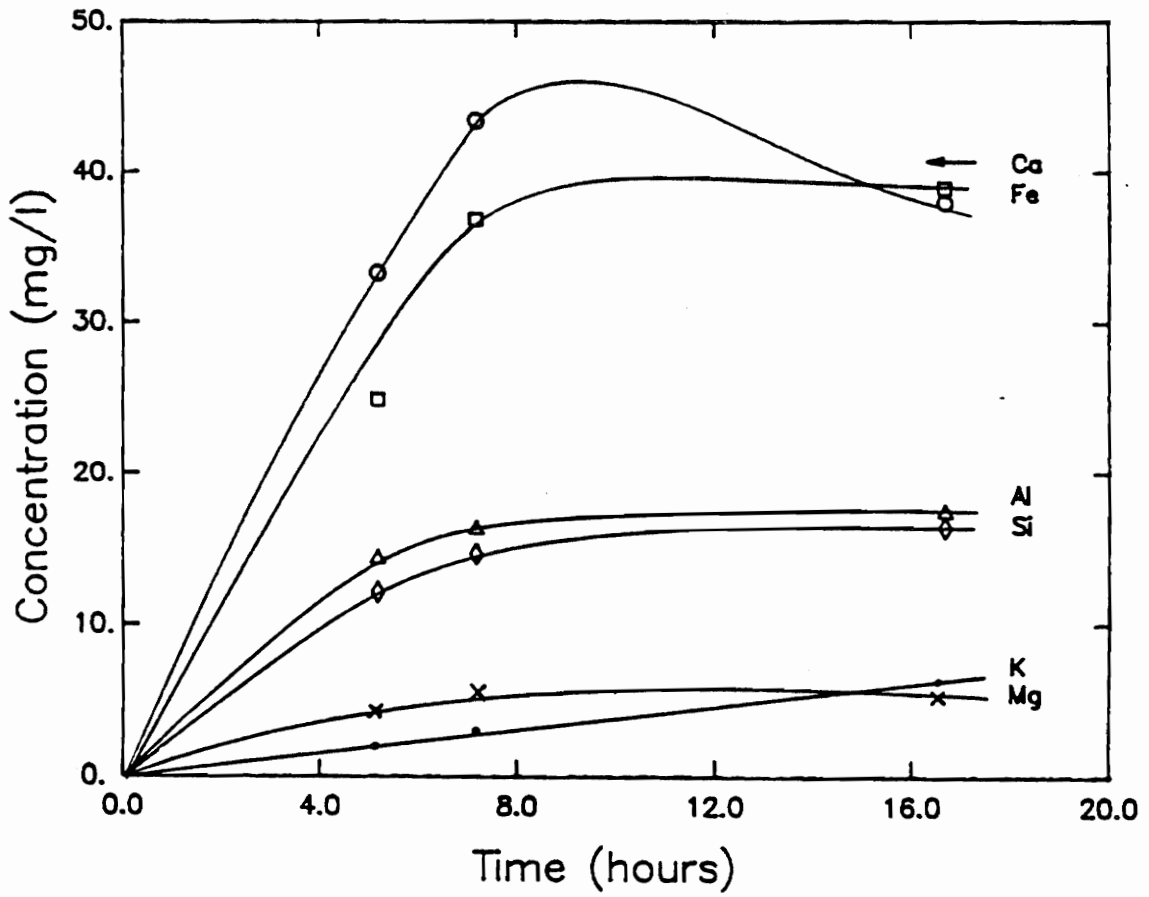


Figure 30. Elements Dissolved by EL in the Column from Floated WK Dominion #1

mostly found in vitrinite or among the clay flakes as framboids, or in fusinite as simple crystal inclusions (picture 1 in Figure 31).

First Stage Product Coal

The product was generally similar to the feed, but less fines were covering the macerals. Picture 2 in Figure 31 indicates that many pyrite crystals were missing on the top of the framboids. Clays remained on coal, and were identified mostly as illite. The proportion of middlings remained nearly unchanged, and no complete removal of the minerals encrusting the macerals could be observed.

Second Stage Product Coal

Fusinite and vitrinite macerals appeared mostly clear of mineral matter (see electron micrograph 3 in Figure 32). However, clay flakes remained on vitrinite, and middlings were not devoid of their mineral encrustations. Cracks were detected, but only on clean vitrinite, and did not seem to lead to minerals inclusions. Pyrite was well removed, even though some framboids were still encrusted in macerals or clays. Picture 4 in Figure 32 shows a middling particle covered by a clay shell, itself holding pyrite. The numerous black holes observed are the sites vacated by the pyrite crystals extracted by the process.

Chlorine was detected on the sample by the EDAX microanalyzer (especially on clay minerals), which may be due to the inefficient rinsing of the acid; this was confirmed by the bright appearance of the sample.

5.1.2.6 Scanning Electron Microscopy on Widow Kennedy Dominion #1

This floated coal was treated with EL in both the elutriation column and the reaction vessel. The feed treated in the column was assaying 3.45% ash and yielded a

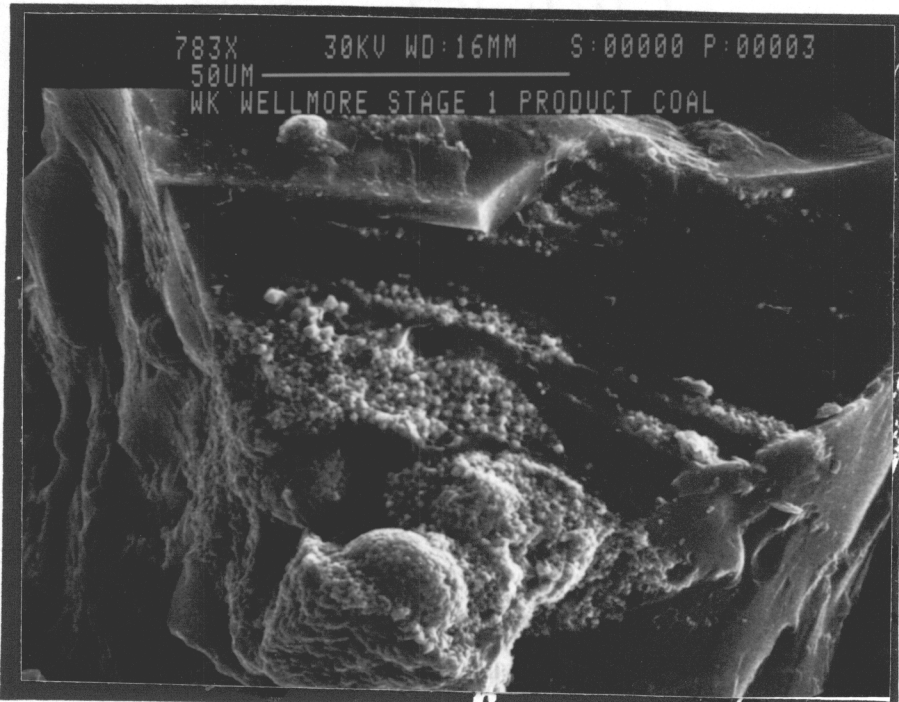
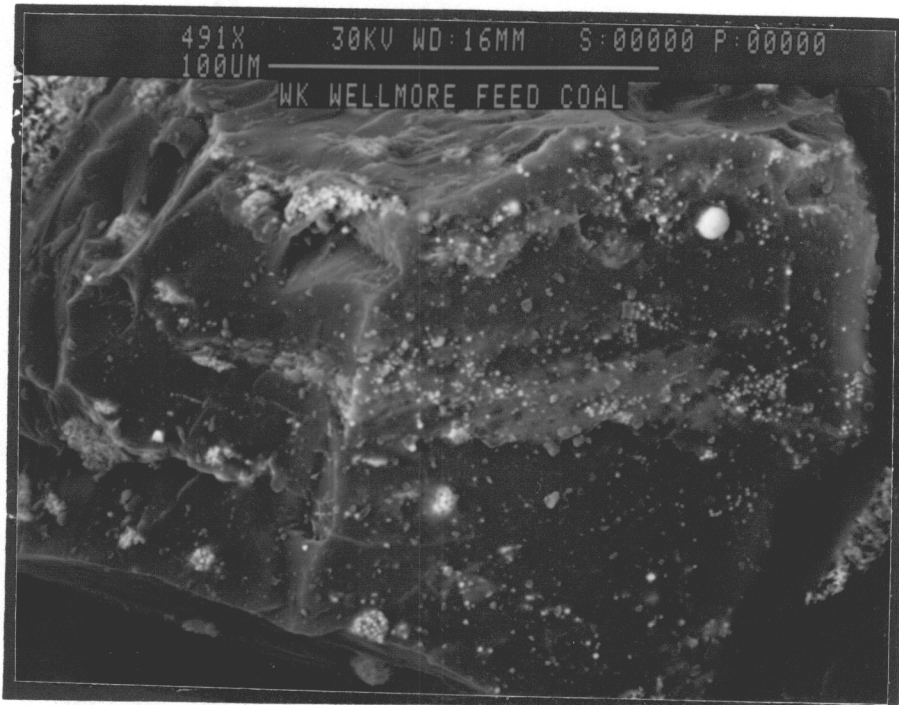


Figure 31. Electron Micrographs of Widow Kennedy Wellmore: *Above:* 1 Feed Coal with Pyrite and Clay Inclusions - *Below:* 2 First Stage Product Coal with Pyrite Framboid

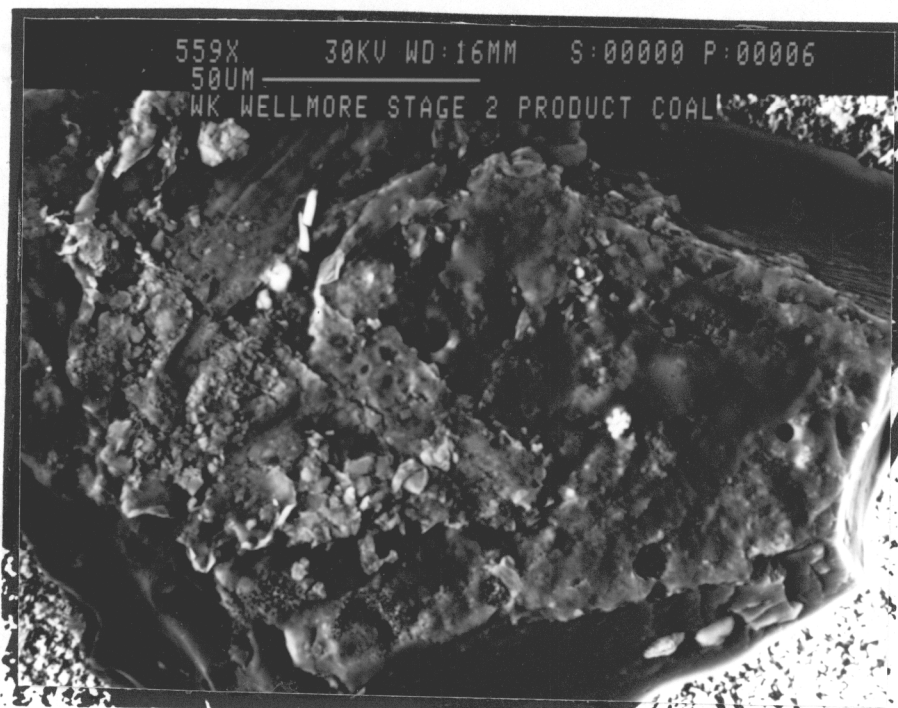
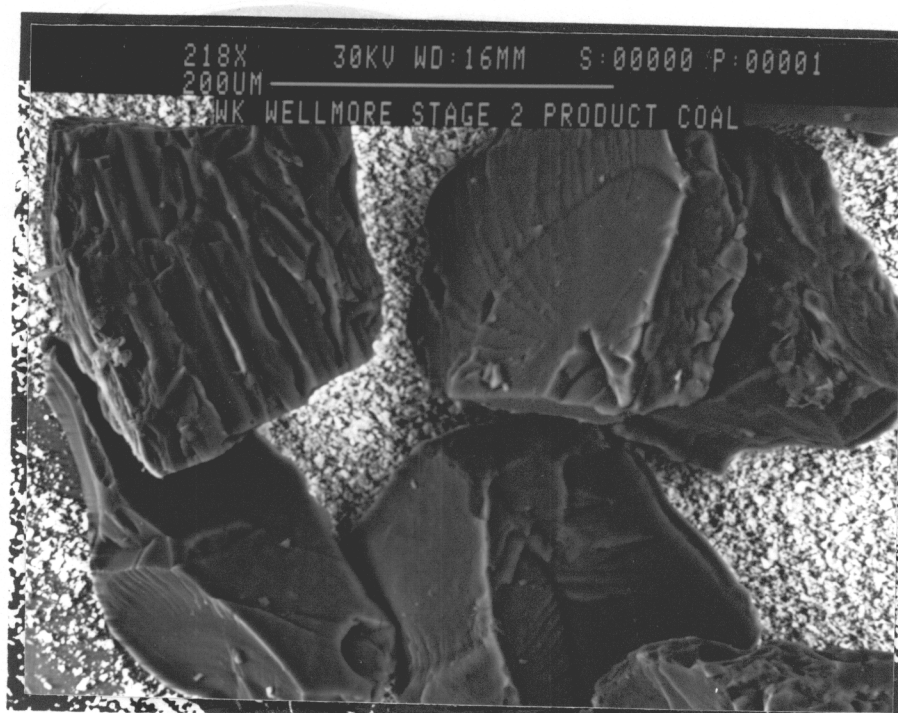


Figure 32. Electron Micrographs of WK Wellmore Second Stage Product: Above: 3 Clean Macerals - Below: 4 Middling with Clay Flake and Pyrite Prints

2.43% ash product (after 30g were subjected to EL for 7 hours and 10 minutes at 53°C in one liter of 15.5%-13.5% H₂SO₄-HCl mixture). The 22.7g feed processed by EL in the vessel, assaying 3.38% ash, yielded a 1.66% ash product (after 10 hours at 60°C in 500ml of the same acid mix).

Run-of-mine Coal

Vitrinite was the major maceral found in the run-of-mine. The unwashed grains were covered with many 1-10µm minerals characterized as illite and kaolinite, as shown in picture 5 in Figure 33.

Floated Feed Coal

Although most adhering minerals were removed by wet-screening followed by flotation, some remained on the particle surfaces. However, many clay flakes were found imbedded in vitrinite, especially at the edges of the grains; this is illustrated by picture 6 in Figure 33 showing the flake-shaped structure of kaolinite on coal. Pyrite framboids extruding from the coal matrix are extremely numerous, as shown in picture 7 in Figure 34, and cracks containing pyrite are sometimes found.

LT Ash from Floated Feed

The major compounds visible in the LT ash were clays and pyrite. Clays were found as individual grains or mixed with unburned coal. Pyrite framboids are remarkably revealed by picture 8 in Figure 34, as regular spheres of 5 to 20µm in diameter, made of aggregates of numerous 1-2µm sharp-edged cubic crystals.

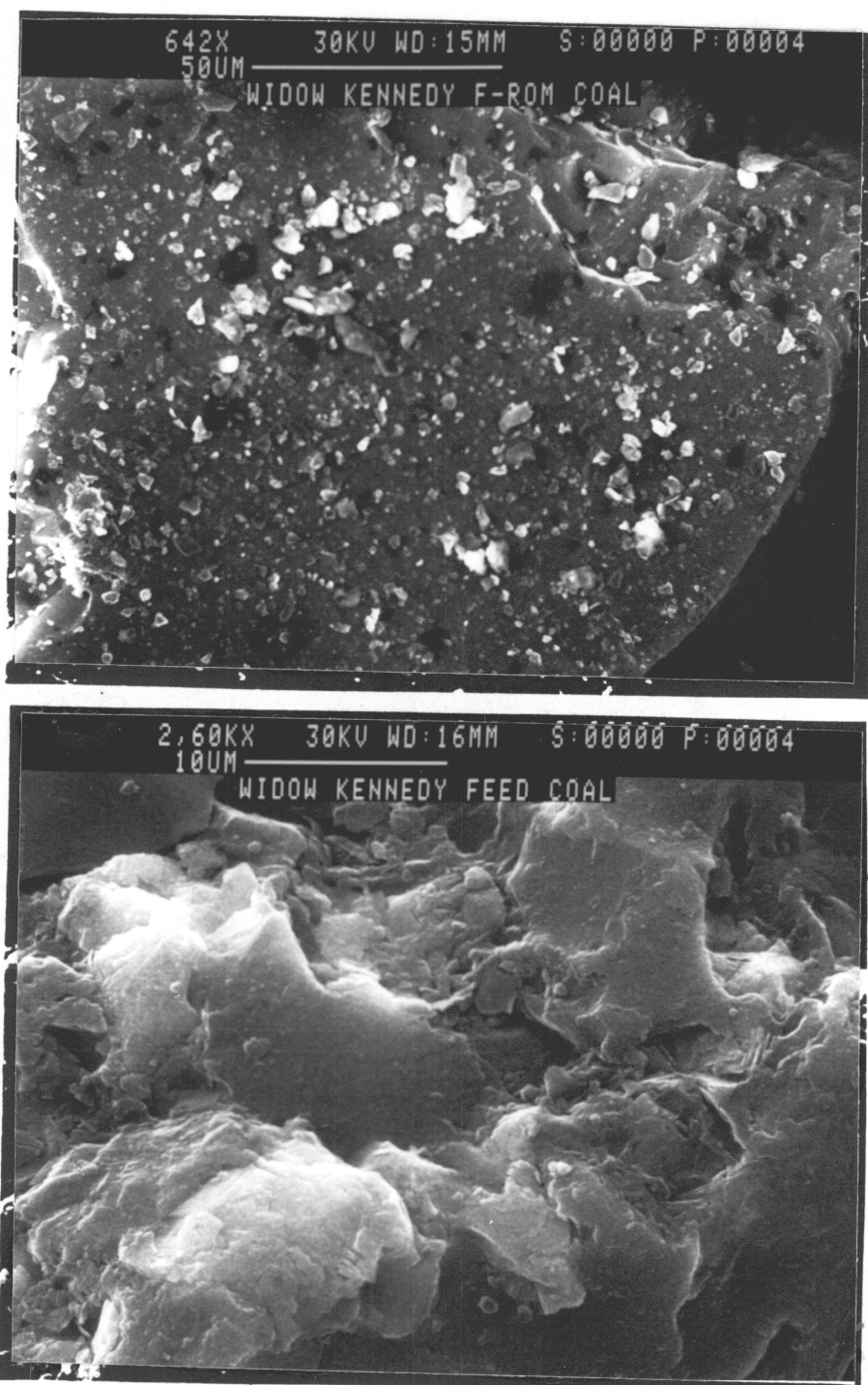


Figure 33. Electron Micrographs of Widow Kennedy Dominion #1 Feed Coal: Above: 5 Run-of-mine - Below: 6 Kaolinite on Floated Coal (Brighter Area)

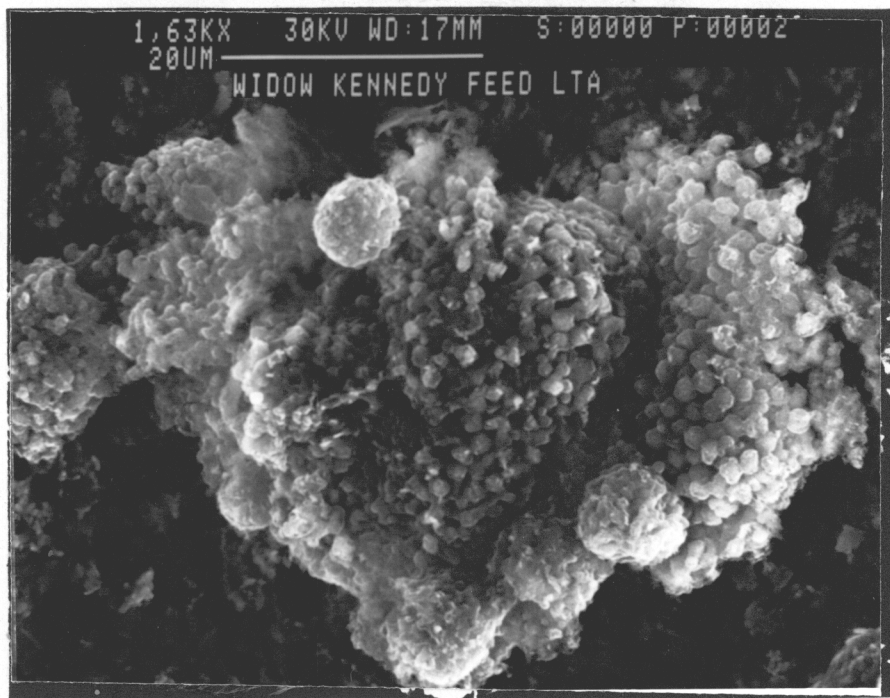
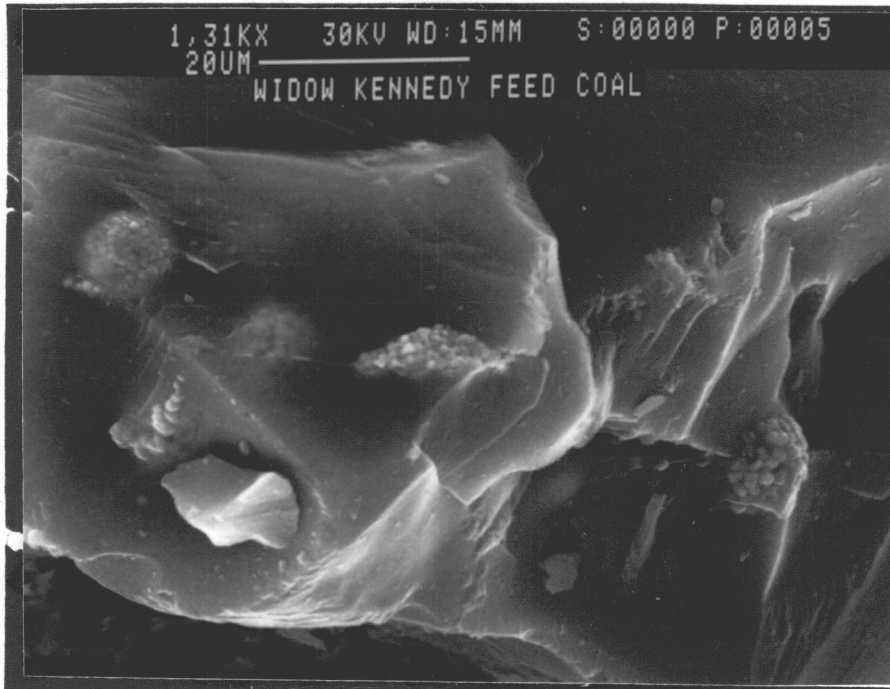


Figure 34. Electron Micrographs of Pyrite in WK Dominion #1 Floated Feed: *Above:* 7 Vitrinite and Pyrite Framboids - *Below:* 8 Pyrite Framboids in LT Ash

Product Coal from the Elutriated Column

All grains were devoid of the adhering minerals which were still noticed in the physically cleaned feed. However, some clays were still remaining encrusted in the surface (micrograph 9 in Figure 35). Cracking was observed in some places. Pyrite was well removed from the surface, picture 10 in Figure 35 indicates that most crystals left their sites empty, proving liberation or total dissolution in situ. However, some pyrite inclusions could not escape from the matrix, as observed on picture 10. The included crystal appears eroded, which suggests that part of the pyrite was dissolved. Finally, anhydrite was frequently detected on the surface.

Product Coal from the Stirred Vessel

The product was similar to the one treated in the column, except that pyrite seemed better removed, and cracking was more noticeable. Stirring and longer processing time may be mainly responsible for these differences which reflect the differences found in the ash contents of the respective products. Pictures 11 and 12 in Figure 36 show a complete removal of pyrite crystals from the coal surface, and their empty sites left on the maceral.

LT Ash from the Stirred Vessel Product Coal

The physical appearance of the product LT ash did not differ much from the one of feed LT ash. As a result, no important conclusion about the product LT ash could be drawn.

Underflow from the Elutriated Column

Free clay particles were present in the underflow from product screening, along with free pyrite crystals that were not totally dissolved. This clearly indicated that some lib-

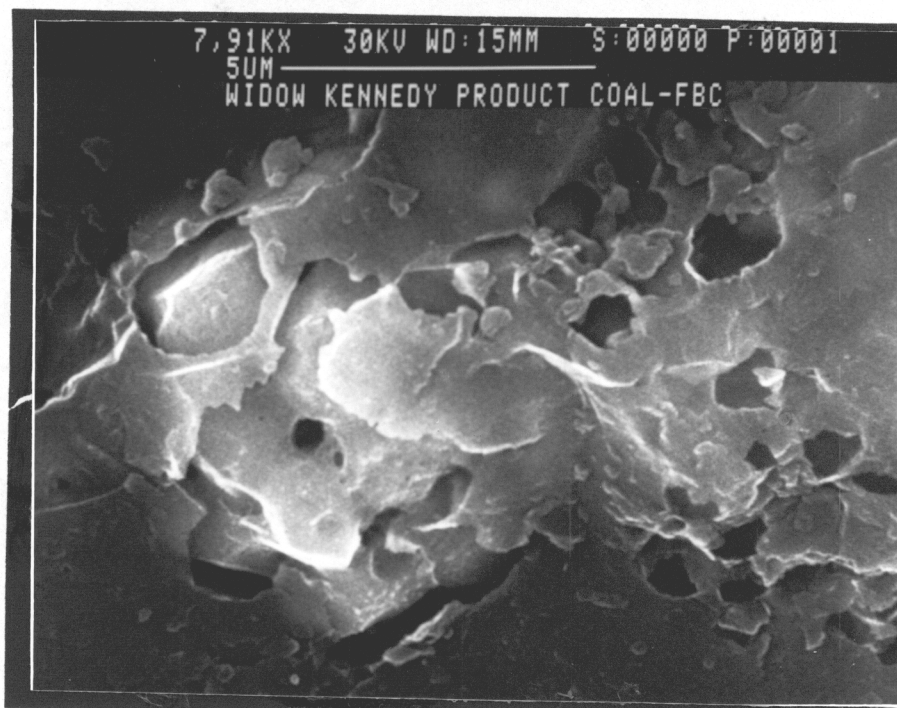
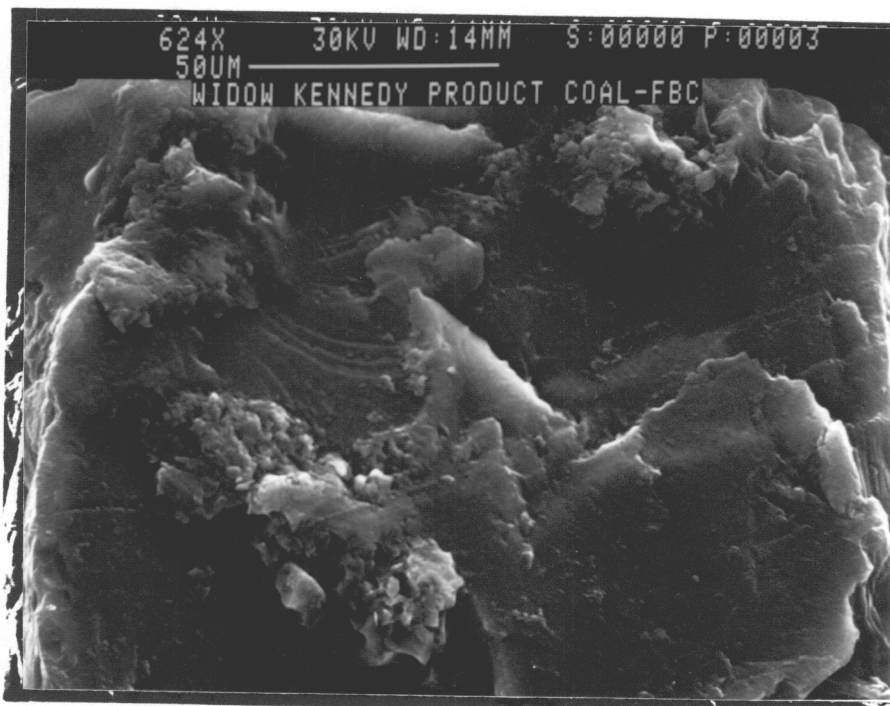


Figure 35. Electron Micrograph of WK Dominion #1 Column Product: *Above:* 9 Vitrinite and Clay Flakes - *Below:* 10 Pyrite Prints and Inclusion

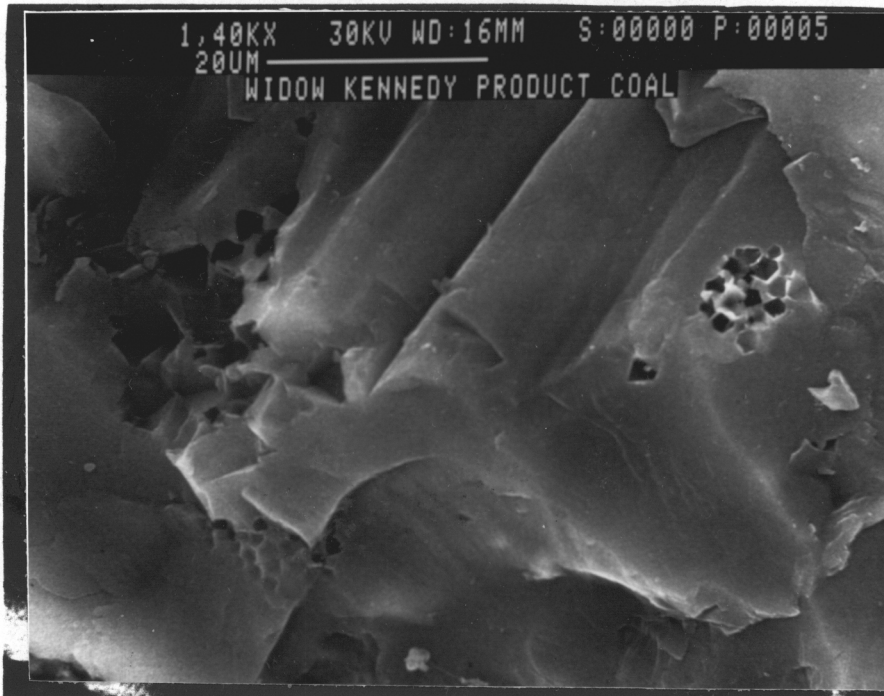
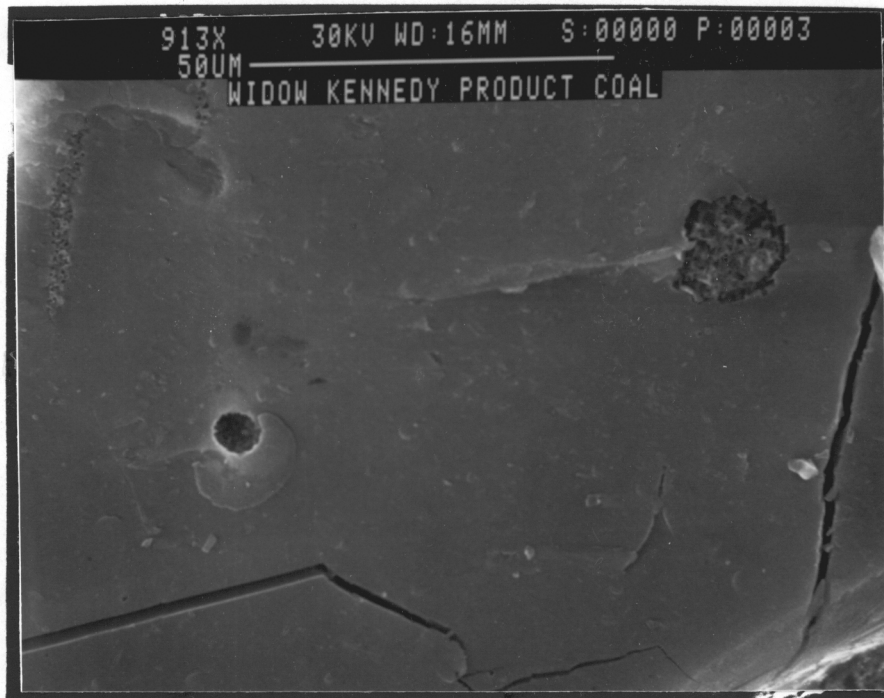


Figure 36. Electron Micrographs of WK Dominion #1 Stirred Vessel Product: Above: 11 Fissures and Pyrite Prints - Below: 12 Pyrite Prints in Vitrinite

eration had taken place on these mineral compounds. Sphalerite was also found as extremely fine bodies.

5.2 Interpretation of the Results

All the analyses conducted so far on the feed and product, in both solid and liquid phases, indicated that the removal of mineral matter was achieved by both dissolution and liberation. However, the results were dependent on the coal tested and also the operating conditions applied.

5.2.1 Suggestions for the Mechanisms of Liberation

Wet-screening the feed coal prior to the CECC was found to be very important. The ash content decreased by 33% when a run-of-mine Jacob's Ranch coal was wet-screened. This accounted for 45% of the total removable ash removal from this coal. This way, the wet-screening reduced the ash by 14% from a Splashdam coal, 25% from a high ash Widow Kennedy coal, 25.6% from a Pittsburgh #8 coal, and 15% from a low ash Widow Kennedy coal. It was very clear from the mass balance calculations that the less the coal was washed or physically cleaned, the higher was the proportion of mineral matter in the underflow; most of this mineral matter liberated as such could be attributed not to liberation in the true sense of the word, but to simple detachment of fine particles from the coarse. However, the latter mechanism may also be called "liberation" in a much broader sense.

1) The first minerals to be liberated would be the ones remaining on the feed coal surface despite the wet-screening. SEM study did reveal that the feed surface was not perfectly clear of these fine adhering minerals. Liberation of these bodies would certainly be favored by the acid treatment, the liquid heat and the mechanical stirring of the slurry.

2) The most interesting explanation is the mechanism of opening of cracks in the coal matrix or between minerals by osmotic pressure. According to the model recently proposed by Paul (1988), an osmotic pressure can develop by the interaction of two double layers in close distance. The osmotic pressure is essentially the same as the electrical contribution to the disjoining pressure. This pressure may be strong enough to weaken the contacts between coal and mineral matter inducing liberation. Van Olphen (1977) noted that the osmotic pressure can be as high as several tens of atmospheric pressure. The osmotic pressure may also operate in "liberating" slime particles from coal particles.

Pyrite inclusions in product coal, when observed at a high magnification, were most of the time found imbedded in a maceral opened by small crevices. Also, space was often noticed between these inclusions and the surrounding maceral walls, which should favor the leaching of the mineral. However, these small detected fissures did not seem to be wide enough to allow mineral matter to escape or liberate from coal readily. It is possible that these cracks could have been created by the osmotic pressure.

The empty sites left by framboidal pyrite crystals on the product Widow Kennedy vitrinite may be an evidence of pyrite crystals liberation by the osmotic pressure. For Jacob's Ranch coal, the silicate plates located on the surface may have been liberated by the osmotic (or disjoining) pressure between the coal and the mineral. These obser-

vations fit the osmotic pressure theory, although it is difficult to prove that this was the only mechanism involved.

Predictions from the model of osmotic pressure were presented by Paul (1988). According to the model, the osmotic effect should be dependent on the surface porosity of the coal. The ideal surface would be a rough surface offering numerous sites favorable to double layer overlapping. In addition, the pore size should fall within the range allowing high pressure. Typically, pressure should vary between 1 and 30 atm for pore diameter of 50 to 1000Å, the smaller spacing inducing the higher pressure. Below 10Å or above 1000Å, the model is not applicable.

Paul (1988) suggested that the coal surface is expected to become more positively charged by the presence of ferric ions in the electrolyte, which superficially oxidizes the coal surface. In the present work, the addition of ferric ions did not improve liberation significantly, but the zeta potential could not be measured because of the pH. It should be noted, however, that ferric ions were already present in the system, which have made it difficult to see the effect of extraneously added ferric ions. Paul's model also showed that an increase in electrolyte concentration should increase the osmotic effect, for an increase in sulfuric acid concentration from 0.1 to 1M, the pressure should increase by 30%.

The osmotic pressure mechanism may actually operate on many localities on coal but direct evidence is difficult to obtain. Nevertheless, the clean removal of pyrite framboids, as shown by SEM photographs, supports the osmotically induced liberation theory.

3) Relatively insoluble minerals may be cemented to the coal surface by some fine soluble mineral matter. The dissolution of this mineral matter will easily disjoin those minerals from the coal and from other minerals. This might be the case for framboidal

pyrite crystals, since they are often cemented by fine pyrite powder (Renton, 1982). However, no evidence is given for this in the present work.

The same may be the case for silicates, which are held inside the fusinite pores by carbonates. However, these silicate platelets seemed to be retained inside the pores, probably due to their morphology.

4) It is also possible that chemical dissolution would reduce the size of mineral grains, loosen it from the coal, and then liberate them. In this case, not all the mineral matter found in the underflow should be ascribed to the osmotic liberation mechanism. This may also explain why coal reduced in size is present in the tailing.

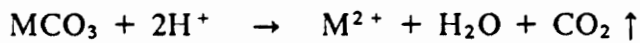
5.2.2 Suggestions for the Mechanisms of Dissolution

1) Mineral matter could be dissolved by the reagent directly contacting the surface, the pores and the crevices. Mineral matter dissolution should depend on thermodynamic, as well as on kinetics.

- Kinetics should depend on the chemical nature of mineral matter and on its accessibility, as well as on experimental conditions. Soluble species, like calcite and dolomite could dissolve in half an hour, while less soluble minerals, such as pyrite and clays, did in 10 hours. Cracking by osmotic pressure should enhance acid diffusion, and hence dissolution. Other parameters that affect dissolution would include temperature, oxidation potential, number of cleaning stages, etc.

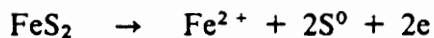
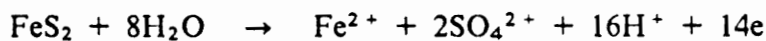
- In terms of thermodynamics, all the minerals are more or less soluble in acid, depending on the acid strength. At low pH, the following reactions may take place:

1. *For carbonates*, the following reaction may represent the general mechanism,

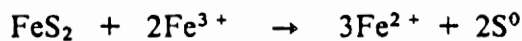


in which M represents metal ions such as Ca, Mg and Fe.

2. *For pyrite*, the following oxidation mechanisms may apply:



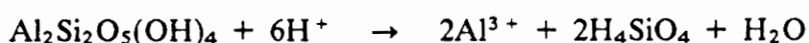
The ferrous ions will be oxidized to ferric ions if the potential is kept above the equilibrium potential of the reaction. The ferric ions in turn act as a leaching medium for pyrite as follows:



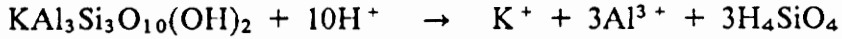
It has been shown that, by applying a 1v potential on a platinum working electrode immersed in the coal slurry, the sulfur removal from Widow Kennedy coals was improved.

3. *For kaolinite* :

Silicates are not very soluble in aqueous solution; however, aluminosilicates become hydrated according to various mechanisms. Kaolinite can release hydrated aluminum ions in different ways (Huang and Keller, 1973): Al^{3+} , $2\text{Al}(\text{OH})^{2+}$, $2\text{Al}(\text{OH})_3^+$ and $2\text{Al}(\text{OH})_4^-$. The stability field of kaolinite strongly depends on pH for pH below 6. Since the process involves very low pH, the most likely reaction to occur may be:

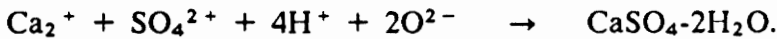


4. For illite, the following mechanism may apply:



2) Minerals freshly extracted from the coal matrix are necessarily undergoing leaching in the slurry. Liberated minerals such as clays and pyrite crystals should therefore contribute to the dissolution of the species quantified by elemental analysis.

3) Analyses of leachates suggested precipitation of calcium-containing minerals. It is possible that gypsum precipitates according to the following reaction:



The solubility limit of gypsum is 0.015M (Nebergall et al., 1972). Precipitation of carbonate may also be possible:



It is interesting to note that the solubility of every type of calcium sulfate decreases with increasing temperature. Between 30 and 100°C, the solubility of gypsum varies from 2.4g/l to 2.2g/l, the anhydrite one from 2.1g/l to 1.6g/l and the bassanite one from 3g/l to almost zero (CRC Handbook, 1981). This may explain why the dissolution of calcium was inhibited, and why precipitation was observed at high temperature.

4) Opening of cracks or swelling of clays due to osmotic pressure could favor the penetration of electrolytes (or acids) inside the coal structure, and thereby increase the leaching rate. Although hydration and swelling of clays probably occurred, no complete removal was observed. Van Olphen (1977) stated that the swelling of clays was limited by cohesion forces, known as cross-linking forces (positive edge-negative face) and Van der Waals attraction forces.

5) Finally, it has been demonstrated that the proportion of mineral matter liberated and dissolved can be calculated by two methods. The mass balance calculated from solid weights provides more direct measurements of the liberated matter contained in the underflow. This method is more reliable, provided that all the slimes coating coal particles are removed before processing. The mass balance calculated from the leachate is less reliable because only a few minerals are taken into account, and also because the many assumptions (refer to appendix C). Despite discrepancy between the two methods of mass-balancing, there was a reasonable correlation between them.

5.2.3 Statement on the Process Mechanisms

No single general theory can explain the way mineral matter is removed from coal. Rather, each type of mineral seems to be subject to one or several specific mechanisms, depending on its chemical nature, morphology and mode of occurrence. Similarly, the chemical nature and the morphology of the maceral is expected to affect the removal of its mineral matter.

6.0 CONCLUSIONS

6.1 *Review of the Study*

1. The CECC process aimed at cleaning coal from its mineral matter could achieve good ash reductions. Up to 70% of the mineral matter could be removed from a feed coal previously wet-screened under relatively mild operating conditions. The wet-screened Jacob's Ranch coal assaying 6% ash could be cleaned by the CECC to 2% ash at the 62-210 μ m particle size range. No physical cleaning process was effective in removing the mineral matter from this coal because the major constituent of the coal is fusinite and most of the minerals are encapsulated inside the tubular pore structure. The CECC process removes a substantial portion of this mineral matter under relatively mild acid conditions.

It was found that 33% of the mineral matter contained in a run-of-mine sample could be removed by simple wet-screening. The majority of the mineral matter removed as such were quartz and illite. Therefore, if the CECC process is run without careful wet-screening, erroneous interpretation of the results may follow.

2. Application of an oxidizing potential through a working electrode immersed in a coal slurry improved the reduction of mineral matter, especially that of pyrite. It is considered that ferrous ions derived from pyrite and other iron-containing mineral matter were oxidized to ferric ions on the working electrode, which in turn creates an osmotic pressure which may improve the mineral liberation. It is likely that the ferric ions acted as a leaching medium for the pyrite. During this process, ferric ions were reduced to ferrous ions, which could then be oxidized back to ferric ions as long as the redox potential of the system was above the reversible potential of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ couple. However, extraneous addition of ferric ions to the system was not found to be effective in further improving the CECC process. The reason may be that there was already enough ferrous ions derived from the mineral matter contained in the coal.
3. Higher temperature did typically enhance the removal of mineral matter. It particularly enhanced the removal of less soluble species, such as silicates and pyrite. However, a low temperature was preferred to dissolve the carbonate species.
4. Sulfur content was well reduced by the CECC process, especially for the coals containing substantial amount of pyrite. Up to 22.6% of sulfur removal was observed on the Widow Kennedy Dominion #1 coal. On the contrary, the sulfur rejection from the Jacob's Ranch and the Wyodak coals was poor because these coals contain bassanite, which is not readily soluble in acid, as the major sulfur-containing mineral. Finer grinding should improve the removal of pyrite, because it will enhance the exposure of the crystals to the solution.
5. Physical coal cleaning processes such as froth flotation and dense medium separation may be more efficient in removing mineral matter to a relatively low ash and

pyritic sulfur level. The CECC process will be useful in further reducing the ash and sulfur level beyond the limits of the physical cleaning processes.

6. From this study, the most important mechanism governing the CECC process was found to be dissolution. From 57% to 94% (depending on the coal feed purity and the treatment) of the mineral matter was removed from the Widow Kennedy coal by dissolution, and even a larger percentage from Jacob's Ranch coal, the balance being due to liberation. The proportion of dissolved mineral matter was higher than what was reported by Paul (1988), which may be attributed to the fact that considerably higher acid concentrations were used in the present work.

Elemental analysis of the solution showed that the most soluble species were removed within a short period of time, i.e. from 15 to 30 minutes at room temperature. Up to 90% of the mineral matter removed from a Wyodak coal in 4 hours was removed within the first half an hour. Another test conducted on the Jacob's Ranch coal demonstrated that 90% of the mineral matter extracted in one hour and half was removed by dissolution only. Dissolution of soluble mineral matter was not limited to those on the coal surface; SEM studies showed that considerable amounts of mineral matter inside the pores of fusinite were dissolved.

Less soluble species also responded to dissolution, but at lower rates. Pyrite could be eroded by leaching, and silicates were released in noticeable amounts. However, longer treatments were required (about 10 hours) along with higher temperature (60°C) to reach good results.

Precipitation phenomenon was commonly observed with calcium, especially with strong acid and at high temperature. It falsified the concentration of dissolved elements, hence the mass balance on leachates. Calcium could precipitate into gypsum and increase the sulfur content of the product (if sulfuric acid is used). To

avoid lowering process efficiency due to precipitation, a multistage treatment, using fresh acid at each stage, was designed and thereby improved the removal of soluble minerals.

7. Considerable amounts of mineral matter were also removed by liberation phenomena, which may involve several mechanisms. First, swelling, disjoining and cracking of solids due to osmotic pressure could induce liberation as well as enhance the dissolution of less soluble mineral matter; these effects were observed with the SEM at the coal-pyrite interface. However, the liberation of silicates was not clearly observed in this study.

With the low-rank coals studied in the present work, some clays and quartz were mixed with calcite and dolomite inside the pores of fusinite. SEM photographs show evidence that these carbonates were selectively dissolved, which may result in the "liberation" of the insoluble mineral matter. It has been found, however, that much of the quartz and the kaolinite was remaining inside the pores.

6.2 *Future Work*

More fundamental studies are necessary to elucidate the mechanisms involved. As in the past, experimental work shall be the best way to check the validity of theoretical models.

6.2.1 Quantification of the Process

The various mechanisms met in dissolution and liberation of mineral matter deserve more attention. It is necessary to evaluate the participation of each mechanism in the whole process. For example, this evaluation would require examination of a single coal particle step by step, as it is undergoing the CECC process. At each step, SEM studies should be carried out to monitor the changes in morphology of both coal and mineral matter. Since the opening of pores and cracks by osmotic pressure will increase the surface area, specific surface measurements with CO₂ adsorption technique would be useful. Although the present study showed that chemical dissolution plays an important role in the CECC process, the mechanism of mineral matter removal by osmotic pressure requires further consideration. It would be useful to carry out the CECC process without acid, so that one can observe only the liberation process without being obscured by the chemical dissolution.

It would be also interesting to determine how much of each mineral is undergoing liberation, as it was done in this study for dissolution. This way, the efficiency of the CECC process would be evaluated, particularly for the removal of pyrite, kaolinite, illite and quartz, which are not very soluble minerals.

6.2.2 Improvement of the CECC Process

The work on the multistage process, including stages specially designed to improve liberation should be encouraged. Next, the optimization of the separation process would also be a key of the future work; for example, a more efficient rinsing would better extract chlorine and sulfates still present in products after separation from the leachate.

Then, the application of ultrasonic treatment to the slurry before the separation phase should be considered very seriously to complete initiated liberation, such as the removal of the silicate plates contained in fusinite pores.

The treatment of finer particles should be considered with attention. The removal of pyrite from Widow Kennedy vitrinite should increase with decreasing particle size, and so will the removal of other minerals.

Then, the recovery of the overall process should be optimized by working through the different fractions of the coal. For example, the fraction of coal treated by flotation, e.g. 50-300 μm , could be further cleaned with the CECC process; the coarse coal particles could be recovered by heavy media separation, reground and then subjected to the process. As for fines, they could be first physically cleaned by microbubble flotation, and then treated by the CECC process.

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Appendix A. Leachate Analyses for Jacob's Ranch

Experimental Design

Test # 01	1/2h	1h	2h	3h	4h	
Potassium	7.5	7.5	7.2	7.8	8.2	mg/l
Aluminum	94	105	115	129	139	mg/l
Silica	9.4	8.1	9.1	8.4	9.7	mg/l
Magnesium	177	193	181	198	201	mg/l
Calcium	893	977	903	1080	1070	mg/l
Iron	322	352	374	416	434	mg/l

Test # 02	1/2h	1h	2h	3h	4h	
Potassium	18.0	19.0	18.0	19.0	19.0	mg/l
Aluminum	206	238	253	270	273	mg/l
Silica	10.1	8.9	12.9	15.0	9.4	mg/l
Magnesium	479	505	486	464	497	mg/l
Calcium	754	1220	988	767	871	mg/l
Iron	508	572	558	594	664	mg/l

Test # 03	1/2h	1h	2h	3h	4h	
Potassium	7.3	7.0	7.4	7.3	7.2	mg/l
Aluminum	97	109	122	128	139	mg/l
Silica	9.6	8.3	8.3	9.0	8.5	mg/l
Magnesium	163	172	166	173	179	mg/l
Calcium	913	831	910	908	924	mg/l
Iron	606	622	642	638	644	mg/l

Test # 04	1/2h	1h	2h	3h	4h	
Potassium	16.0	18.0	17.0	18.0	17.0	mg/l
Aluminum	187	237	253	372	353	mg/l
Silica	11.1	10.9	10.6	9.2	9.4	mg/l
Magnesium	391	444	426	464	461	mg/l
Calcium	1260	1030	829	854	764	mg/l
Iron	722	842	832	878	846	mg/l

Test # 05	1/2h	1h	2h	3h	4h	
Potassium	6.5	6.7	8.8	7.3	7.6	mg/l
Aluminum	91	107	141	150	164	mg/l
Silica	7.0	6.3	6.2	6.4	6.1	mg/l
Magnesium	177	181	197	202	217	mg/l
Calcium	508	223	295	256	425	mg/l
Iron	300	324	356	368	402	mg/l

Test # 06	1/2h	1h	2h	3h	4h	
Potassium	16.0	18.0	18.0	18.0	18.0	mg/l
Aluminum	223	266	358	395	431	mg/l
Silica	6.3	6.7	5.6	6.0	6.1	mg/l
Magnesium	430	501	491	493	514	mg/l
Calcium	320	243	282	232	245	mg/l
Iron	438	602	640	666	694	mg/l

Test # 07	1/2h	1h	2h	3h	4h	
Potassium	7.2	5.9	7.1	7.3	6.9	mg/l
Aluminum	104	109	147	158	163	mg/l
Silica	6.3	6.8	6.8	6.8	6.5	mg/l
Magnesium	180	163	194	198	195	mg/l
Calcium	402	433	437	307	326	mg/l
Iron	612	576	558	684	688	mg/l

Test # 08	1/2h	1h	2h	3h	4h	
Potassium	1.22	16.0	18.0	18.0	18.0	mg/l
Aluminum	181	305	386	394	419	mg/l
Silica	7.2	6.4	6.3	6.9	7.8	mg/l
Magnesium	333	459	507	475	480	mg/l
Calcium	270	239	214	218	253	mg/l
Iron	638	872	992	962	982	mg/l

Test # 09	1/2h	1h	2h	3h	4h	
Potassium	7.4	6.5	8.35	8.1	7.7	mg/l
Aluminum	150	134	193	191	185	mg/l
Silica	7.9	9.0	8.8	9.7	9.7	mg/l
Magnesium	186	151	224	210	197	mg/l
Calcium	450	540	527	318	288	mg/l
Iron	388	336	444	430	406	mg/l

Test # 10	1/2h	1h	2h	3h	4h	
Potassium	17.2	17.4	17.1	18.7	21.4	mg/l
Aluminum	350	388	407	459	529	mg/l
Silica	10.3	12.8	14.3	14.4	14.3	mg/l
Magnesium	412	424	422	476	366	mg/l
Calcium	878	640	875	624	519	mg/l
Iron	642	684	686	756	864	mg/l

Test # 11	1/2h	1h	2h	3h	4h	
Potassium m	7.4	8.0	7.6	8.2	10.3	mg/l
Aluminum	158	186	189	201	245	mg/l
Silica	11.9	10.2	11.4	11.3	11.6	mg/l
Magnesium	133	153	144	150	185	mg/l
Calcium	479	543	467	560	555	mg/l
Iron	652	718	692	698	834	mg/l

Test # 12	1/2h	1h	2h	3h	4h	
Potassium	14.2	15.2	16.4	14.8	17.9	mg/l
Aluminum	296	349	406	376	456	mg/l
Silica	11.4	13.2	10.7	12.5	11.9	mg/l
Magnesium	354	383	442	378	464	mg/l
Calcium	997	895	975	872	742	mg/l
Iron	806	884	992	880	1054	mg/l
Test # 13	1/2h	1h	2h	3h	4h	
Potassium	6.9	7.2	7.6	7.9	7.3	mg/l
Aluminum	172	175	203	202	214	mg/l
Silica	8.4	9.2	7.4	10.2	7.6	mg/l
Magnesium	121	119	131	119	131	mg/l
Calcium	323	349	307	237	326	mg/l
Iron	376	366	412	392	398	mg/l
Test # 14	1/2h	1h	2h	3h	4h	
Potassium	11.1	10.4	10.1	10.9	11.9	mg/l
Aluminum	252	257	265	294	317	mg/l
Silica	7.2	9.1	8.9	8.3	7.4	mg/l
Magnesium	234	215	203	228	248	mg/l
Calcium	261	277	271	245	270	mg/l
Iron	488	458	440	480	510	mg/l
Test # 15	1/2h	1h	2h	3h	4h	
Potassium	9.2	7.4	7.9	6.2	7.4	mg/l
Aluminum	170	184	196	153	201	mg/l
Silica	6.7	7.4	8.8	6.8	6.6	mg/l
Magnesium	120	130	131	100	118	mg/l
Calcium	184	263	252	314	183	mg/l
Iron	698	708	708	554	672	mg/l

Test # 16	1/2h	1h	2h	3h	4h	
Potassium	10.1	12.3	12.6	13.5	14.9	mg/l
Aluminum	249	319	336	356	397	mg/l
Silica	6.9	6.6	7.5	7.7	8.5	mg/l
Magnesium	214	252	280	304	355	mg/l
Calcium	382	234	298	244	217	mg/l
Iron	628	722	772	826	946	mg/l

Test # 17	1/2h	1h	2h	3h	4h	
Potassium	11.9	11.5	11.7	12.5	11.7	mg/l
Aluminum	196	214	237	269	251	mg/l
Silica	8.3	9.4	8.8	10.2	9.3	mg/l
Magnesium	310	300	300	317	293	mg/l
Calcium	582	357	582	390	487	mg/l
Iron	674	654	710	770	690	mg/l

Test # 18	1/2h	1h	2h	3h	4h	
Potassium	11.0	11.8	10.9	12.0	11.6	mg/l
Aluminum	228	278	283	296	309	mg/l
Silica	10.8	10.7	11.0	13.5	9.4	mg/l
Magnesium	207	221	199	210	174	mg/l
Calcium	152	306	347	386	304	mg/l
Iron	594	648	598	614	668	mg/l

Test # 19	1/2h	1h	2h	3h	4h	
Potassium	9.2	9.7	--	10.2	--	mg/l
Aluminum	181	224	--	266	--	mg/l
Silica	8.9	10.7	--	11.0	--	mg/l
Magnesium	164	179	--	201	--	mg/l
Calcium	556	434	--	423	--	mg/l
Iron	468	520	--	582	--	mg/l

Test # 20	1/2h	1h	2h	3h	4h	
Potassium	2.5	2.7	2.9	3.1	3.3	mg/l
Aluminum	40.0	44.0	50.0	53.0	56.0	mg/l
Silica	9.4	9.1	10.4	9.5	9.4	mg/l
Magnesium	32.0	35.4	35.2	39.4	37.0	mg/l
Calcium	239	461	275	284	288	mg/l
Iron	468	568	648	682	704	mg/l

Test # 21	1/2h	1h	2h	3h	4h	
Potassium	23.0	25.0	25.0	25.0	26.0	mg/l
Aluminum	452	514	550	583	596	mg/l
Silica	11.7	9.7	10.5	11.3	9.7	mg/l
Magnesium	620	666	674	708	694	mg/l
Calcium	257	329	405	373	346	mg/l
Iron	934	942	960	1020	2050	mg/l

Test # 22	1/2h	1h	2h	3h	4h	
Potassium	33.0	31.0	12.9	12.6	14.0	mg/l
Aluminum	221	237	272	268	372	mg/l
Silica	11.3	9.7	10.2	10.0	9.5	mg/l
Magnesium	702	664	722	670	808	mg/l
Calcium	620	589	569	632	406	mg/l
Iron	398	412	456	474	564	mg/l

Test # 23	1/2h	1h	2h	3h	4h	
Potassium	11.3	12.1	11.5	9.7	11.0	mg/l
Aluminum	222	260	268	256	171	mg/l
Silica	9.8	9.3	9.5	9.7	9.4	mg/l
Magnesium	646	688	636	626	716	mg/l
Calcium	454	513	572	561	311	mg/l
Iron	960	1040	1020	958	1148	mg/l

Test # 24	1/2h	1h	2h	3h	4h	
Potassium	10.9	11.5	12.1	10.1	10.1	mg/l
Aluminum	119	128	158	175	153	mg/l
Silica	7.5	8.7	7.3	7.9	8.3	mg/l
Magnesium	670	618	678	734	608	mg/l
Calcium	1430	984	806	1090	535	mg/l
Iron	452	422	486	500	434	mg/l

Test # 25	1/2h	1h	2h	3h	4h	
Potassium	11.1	12.3	12.1	12.2	13.0	mg/l
Aluminum	197	231	261	328	360	mg/l
Silica	4.6	5.1	5.1	5.7	5.3	mg/l
Magnesium	654	698	742	738	756	mg/l
Calcium	149	160	137	195	207	mg/l
Iron	568	636	644	704	721	mg/l

Test # 26	1/2h	1h	2h	3h	4h	
Potassium	10.9	8.2	12.3	12.2	11.8	mg/l
Aluminum	129	107	173	190	200	mg/l
Silica	10.5	8.0	10.3	10.5	9.2	mg/l
Magnesium	646	462	656	708	694	mg/l
Calcium	559	537	567	392	298	mg/l
Iron	446	342	534	546	572	mg/l

Test # 27	1/2h	1h	2h	3h	4h	
Potassium	11.5	11.8	12.2	13.7	11.5	mg/l
Aluminum	241	255	353	388	342	mg/l
Silica	9.2	10.2	10.5	12.2	10.8	mg/l
Magnesium	678	680	630	740	722	mg/l
Calcium	461	426	566	389	496	mg/l
Iron	866	912	944	980	868	mg/l

Appendix B. Leachate Analyses for Jacob's Ranch

Optimum Tests

Test M	1/2h	1h	2h	3h	4h	
Potassium	4.0	4.2	4.4	4.2	4.4	mg/l
Aluminum	148.9	167.7	191.2	202.3	212.1	mg/l
Silica	7.0	7.3	7.8	7.3	7.2	mg/l
Magnesium	225.0	228.6	232.2	231.6	232.3	mg/l
Calcium	365.9	353.1	364.3	360.2	357.4	mg/l
Iron	579.2	599.8	614.1	615.9	624.5	mg/l

Test T	1/2h	1h	2h	3h	4h	
Potassium	6.7	6.4	7.7	6.5	6.7	mg/l
Aluminum	293.0	313.1	334.7	347.5	349.6	mg/l
Silica	9.9	7.7	8.9	8.8	9.4	mg/l
Magnesium	318.5	318.0	326.1	329.2	323.9	mg/l
Calcium	763.0	481.8	517.6	445.9	413.9	mg/l
Iron	707.6	727.5	741.7	752.8	747.8	mg/l

Test BT	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	
Potassium	4.5	1.6	1.2	2.1	1.7	mg/l
Aluminum	104.1	18.2	25.4	32.7	7.2	mg/l
Silica	9.9	9.3	8.4	12.2	11.0	mg/l
Magnesium	201.8	5.4	3.0	3.2	1.5	mg/l
Calcium	779.6	131.2	56.3	44.6	19.8	mg/l
Iron	152.6	26.3	33.4	21.5	50.5	mg/l

Appendix C. Conversion from Dissolved Elements into Mineral Compounds

The crystals present in the mineral matter being characterized by x-rays, a list of mineral matter compounds was established. The amount of each compound dissolved was evaluated using the concentration of elements dissolved in the leachate. A formula was derived, based on the ratio of the molecular weights of the element and its corresponding mineral. Assumptions regarding the repartition of the elements in the minerals had to be made, for only six elements were analyzed (K, Al, Si, Mg, Ca and Fe), and distinct minerals could share the same element.

Assumptions

1. All *potassium* was released from *illite* (580.3 g/mole).
2. All *aluminum* left after the balance for *illite* was from the dissolution of *kaolinite* (524.3g/mole).
3. All *silica* left after the balance for *illite* and *kaolinite* was from the dissolution of *quartz* (60.1g/mole).
4. All *magnesium* was from the dissolution of *dolomite* (184.4g/mole).
5. All *calcium* left after the balance for *dolomite* was from the dissolution of 100% *calcite* (100.1g/mole), or of 50% *calcite* and 50% *bassanite* (145.1 g/mole) if *bassanite* was present.
6. All *iron* was from *pyrite* (119.8g/mole), or from *siderite* which had very a similar molecular weight (115.8 g/mole), so that either one could be used for the calculation.

Formula

The mass (or the concentration) of each compound can be derived from the mass (or the concentration) of the corresponding element(s).

Illite : K mg of *potassium* are equivalent to $14.84(K)$ mg of illite.

Kaolinite : A mg of *aluminum* are equivalent to $4.858(A - 2.07K)$ mg of kaolinite.

Quartz : Q mg of *silicon* are equivalent to $2.14[Q - 1.041(A - 2.07K) - 2.155K]$ mg of quartz.

Dolomite : M mg of *magnesium* are equivalent to $7.588(M)$ mg of dolomite.

Calcite : C mg of *calcium* are equivalent to

- $2.497(C - 1.649M)$ mg of calcite if no bassanite
- $1.248(C - 1.649M)$ mg of calcite if bassanite is present.

Bassanite : C mg of *calcium* are equivalent to $1.811(C - 1.649M)$ mg of bassanite if any.

Pyrite : F mg of *iron* are equivalent to $2.146(F)$ mg of pyrite if dominant.

Siderite : F mg of *iron* are equivalent to $2.074(F)$ mg of siderite if dominant.

Vita

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