CHAPTER 3
SAMPLE COLLECTION AND ANALYTICAL METHODS

3.1 Sample collection

Seventy coal and rock samples from the Mae Moh coal mine were collected from recently exposed vertical walls in the northeast, northwest, and central mine pits. Loose surface material was first removed before vertical channel samples were collected. Sample intervals were based primarily on lithology. Coal horizons were frequently split into lower, middle, and upper samples divided either by a claystone- or mudstone-rich zone. Special samples of pyrite and gypsum were collected at various locations.

Samples collected from the northeast, northwest, and central mine pits are listed in Appendix 1. This list includes sample locations and brief sample descriptions.

Table 3.1 Showing the number of samples for geochemical analysis

Geochemical analysis	Types of samples	Number of samples
Proximate analysis	coal	27
Ultimate analysis	coal	27
X- ray diffractometry technique	sediments	30
X- ray fluorescence technique	coal and sediments	52
Induced couple plasma (ICP) technique	coal and sediments	30
Coal petrography study	coal	27
Sulfur isotope study	gypsum and pyrite	15

3.2 Analytical conditions

3.2.1 Sample preparation

All samples were air dried for 3 to 5 days to remove adventitious moisture. After this, samples were crushed by hand in a ceramic mill to an average size less than 2 millimeters. Approximately 0.5 kilogram of each rock sample was milled and homoginized

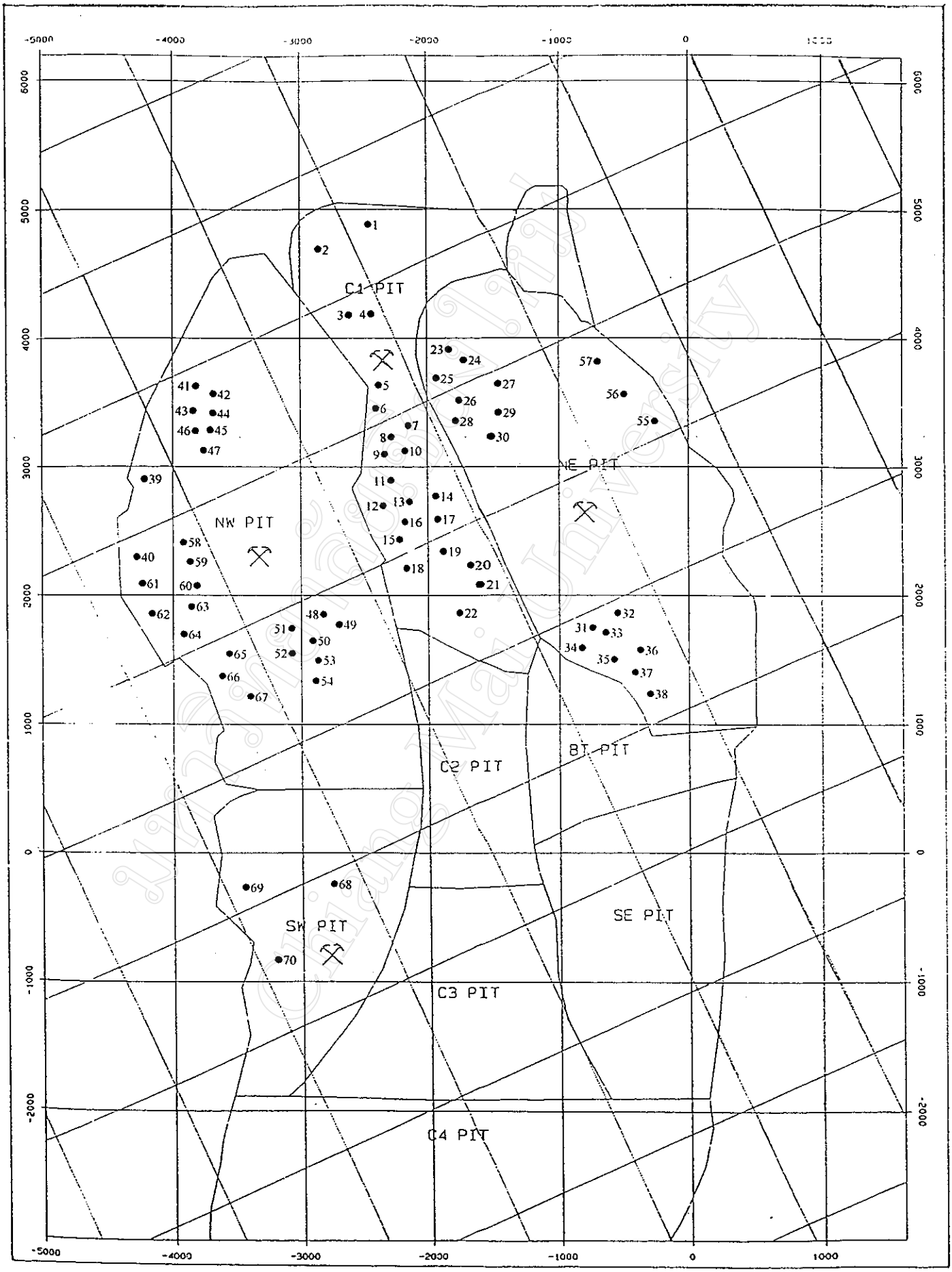

Figure 3.1 Sample location map of Mae Moh coal field

to –200 mesh. These samples were used for x-ray and chemical analyses. Coal samples were milled to –80 mesh and were used for proximate and ultimate analyses and for geochemical characterization. Sample preparation used for the coal petrography and sulfur isotope determination will be discussed later.

3.2.2 Proximate and ultimate analyses

3.2.2.1 Proximate analysis

This analysis determines the amount of moisture and volatile matter and calculates the amount of fixed carbon in coal samples. Procedures follow those described in British Standard, BS 1016, for proximate analysis

-Moisture content

Approximately 1 gram of sample was weigh in a translucent silica dish for moisture determination. This dish was covered and placed in an oven chamber at a temperature of 110^0 C for 1 hour. Following this, the sample was placed in a desiccator and weighed as soon as it was cold to determine the moisture content.

-Ash content

After determining moisture content, the dish with the sample was placed uncovered in a furnace chamber and heated to 900^0 C for 1 1/2 hours. After this, the sample was cooled in a desiccator and then weighed for ash content

Volatile matter content

Approximately 1 gram of sample was used to determine volatile matter content. The weighed sample in a closed translucent silica crucible was placed on supports and inserted into a furnace chamber. The sample was then heated to 900^0 C for exactly 7 minutes. Following this, the crucible was removed from the furnace and, without disturbing the cover, cooled in a desiccator. After this, the cold sample was weighed. The

percentage loss of weight minus the percentage moisture equals the volatile matter content.

Fixed Carbon

Fixed carbon is a calculated value. It equals the sum of moisture, ash, and volatile matter percentages subtracted from 100. All percentages should be on the same moisture reference base.

Fixed carbon percent = 100-(moisture percent + ash percent + volatile matter percent)

3.2.2.2 Ultimate analysis

Ultimate analysis was applied to the analysis of coal and rock samples. The information derived is intended for general utilization by applicable industries to provide the basis for evaluation and beneficiation or for other purposes

In the case of coal and coke, ultimate analysis determines the amount of carbon and hydrogen found in the gaseous products of complete combustion, the amount of sulfur, nitrogen, and ash as a whole, and calculates the amount of oxygen as the difference between 100 and the sum of the other components. Errors can occur if the other components are incorrectly determined and by weight changes of ash-forming constituents when ignited. Oxygen determined by this method as a weight percentage does not include oxygen in minerals or in ash, but it does include oxygen in free water associated with the analyzed sample.

Procedure

Coal samples weighing 0.0002 gram were pre-heated to eliminate moisture. Samples were weighed in a balance that has a precision of 0.000001 gram. After weighing, samples were placed in an aluminum foil cup in a CHNS analyzer furnace (pre-calibration).

3.2.3 X-ray diffraction

The mineral composition of untreated samples of carbonaceous mudstone (coal with >50 percent ash), seam partings, overburden, and underclay was determined by x-ray diffraction.

3.2.3.1 Instrument parameters

Minus 200 mesh samples were pressed onto glass slide holders and analyzed on a rotating anode Rigaku Rotaflex (model RTP 300 Rc) x-ray diffractometer. The diffractometer operated under the following conditions:

- Co K α radiation, 1.790210A^0
- 45 kilovolts and 160 milliamperes
- scans from 2 to 82^0 2θ for untreated samples
- step scan with a counting time of 2 seconds for a step of 0.05^0 2θ

The longer wavelength of cobalt gave better resolution at low angles 2θ than the wavelength of copper and, therefore, gave better definition of the first order clay mineral reflections. The primary beam intensity, which was an order of magnitude higher than conventional x-ray machines, permitted better peak resolution and mineral detection down to approximately 1 percent. Minerals were identified from d-spacings and relative peak intensities using the JCPDS PDF-2 data base retrieval/display system.

3.2.4 X-ray fluorescence spectrometry analyses

X-ray fluorescence spectrometry is a fast and efficient means of determining the concentration of major and trace elements in geological materials

3.2.4.1 Sample preparation

Samples to be analyzed were ashed under standard conditions and ignited to constant weight. Pre-ashed materials were ignited to constant weight under standard conditions. This ash was fused with lithium tetraborate, $Li_2B_4O_7$, and cast onto a glass

disk. This disk was irradiated by a high energy short wavelength x-ray beam. The characteristic x-rays of the atom that were emitted or fluoresced upon absorption of the primary or incident x-rays are dispersed and their intensities at selected wavelengths were measured by sensitive detectors. Detector output is related to concentration by calibration curves or by computerized data handling equipment.

Preparation of coal ash

Coal ash was prepared from a thoroughly mixed representative sample of air-dried coal that had been ground to pass a no. 60 (250-micrometer) sieve. This coal was spread in a layer not over 1/2 inch thick in a fire clay, porcelain, or platinum roasting dish. This dish was place in a cold muffle furnace and the coal sample was heated gradually to 500^0 C in 1 hour and to 750^0 C in 2 hours. The coal was ignited at 750^0 C to constant weight, then cooled and ground to pass a no. 200 mesh (74-micrometer) sieve, and then re-ignited at 750^0 C for 1 hour. Immediately after this, samples must be prepared for analysis or stored in a vacuum desiccator. If samples are stored under atmospheric conditions, they must be reheated at 750^0 C and brought to constant weight before further use.

Preparation of fused sample for analysis

-The powdered sample was first mixed and a portion was weighed and mixed with flux in the ratio of 1.2 grams of sample to 6 grams of flux. This mixture was fused at approximately 1000^0 C in a furnace or commercial fusion device long enough to guarantee complete dissolution of the sample.

- The fusion melt was then be made into a suitable mount by casting the liquid into a mold and forming a glass disk

Preparation of x-ray fluorescence spectrometer

- The manufacturer's instructions for the assembly, conditioning, and preparation of the x-ray fluorescence spectrometer were followed, as well as for control settings and operations.

Calibration and calculations

- Calibration standards were taken from standard reference materials and from synthetically blended pure compounds. The range of concentrations represented by the standards had to exceed the concentration of any unknown element.
- Calculation of elemental concentrations were accomplished by empirical fundamental parameters and by linear regression.

3.2.4.2 Instrument parameters

All samples were analyzed on a Phillips PW 1450 x-ray spectrometer using the following instrumental parameters:

-W tube with a lithium fluoride 200 crystal using both scintillation and flow proportional detectors

- X-ray tube operated at 60 kilovolts and 20 milliamperes

3.2.5 Induced couple plasma analyses

3.2.5.1 Sample preparation

One-tenth gram of each sample was placed in a beaker and treated with a 1 to 1 mixture of hydrofluoric and perchloric acid to dissolve silica components. After drying overnight, the sample was dissolved with a few drops of hydrochloric acid and then diluted with distilled water to a volume of 50 milliliters.

3.2.5.2 Instrument parameters

The samples were analyzed on a SPS 7700 plasma spectrometer using the following parameters:

- Order-sorter pulse-wavelength: 5.000861e-002 degrees
- Echell pulse-angle: 1.526851e-004 degrees
- Filter-in wavelength: 350.000 nanometers
- Photomultiple change wavelength: 540.000 nanometers

- Blaze angle: 63.1376 degrees
- Order-sorter limit pulses: -1319
- Echell limit pulses: 386723
- Maximum raw intensity: 25000
- Minimum raw intensity: 200
- Gain coefficient: 101.206
- Gain offset: 22
- Order-sorter backlash pulse: 1
- Echell backlash pulse: 6

3.2.6 Coal petrography

3.2.6.1 Sample preparation

- Coal briquets were prepared using a binder that held all coal particles securely during grinding, polishing, and observation. After polishing, at least 60 percent of the cross sectional area of each briquet had to be coal.

- Briquets were made by adding an activator, or hardener, and epoxy resin in a ratio of 1 to 5.5 to each sample. This mixture was stirred thoroughly and, initially, a few drops were added to a coal sample that had been placed in a small container. The coal and resin were then stirred thoroughly and more resin was added, a few drops at a time, until all the coal was wet with resin and the coal particles cohered into one mass.

- The internal surfaces of a mold, including plungers, were coated with a release agent. The lower plunger was then inserted and the mold was filled with the coal-resin mixture.

- Briquets were allowed to harden adequately for polishing. Four to eight hours at 35 to 40 degrees Celsius was sufficient for hardening.

- Coal briquets were ejected from the molds using the special attachment on the press. After being ejected, the briquets were labelled.

Preparation of briquet surface

One of the base surfaces of the briquets was ground and polished on a lap to obtain a surface suitable for microscopical examination. Grinding and polishing done by hand manipulation and with an automatic attachment. Both grinding and polishing required several stages to complete. The first stage of polishing was done on a high-speed polishing machine using silicon carbine grit 400 micrometers followed with alumina grit 600 and 1000 micrometers. The second polishing stage was also done on a high speed polishing machine and used chromium oxide and magnesium oxide grit. The third and the fourth stages were done by hand. The polishing media for these two stages was spread out on the cloth of the polishing wheel as a slurry in distilled water.

3.2.7 Sulfur isotope

3.2.7.1 Sample preparation

Nine gypsum and six pyrite samples from four mine pits in the Mae Moh basin were analyzed for sulfur isotope composition. The nine gypsum samples were from the central-1 pit, two pyrite samples were from the southwest pit, two from the northwest pit, and two from the northeast pit. The sulfur isotope analyses were done at the Institute of Geoscience, University of Tsukuba in Japan.

The gypsum samples were dissolved, purified, and subsequently converted to $BaSO_4$ according to the procedure of Kusakabe and Chiba (1983). Preparation of sulfur dioxide gas for the mass spectrometry was made using the cuprous oxide method (Robinson and Kusakabe, 1975). A silver mesh coated with silver sulfide was used directly for this procedure.

Sulfur in pyrite and residual sulfides, however, were first extracted as hydrogen sulfide by the Kiba-regent method (Sasaki and others, 1979). This evolved gas was then converted to silver sulfide via zinc sulfide. Isotopic measurements were made with a McKinney-type mass spectrometer that had a 90° sector and a 20 centimeter radius. Results were expressed in $\delta^{34}S‰$ values.