

II. LITERATURE REVIEWS



2.1 General consideration

Most of airborne trace elements are derived from either natural processes or anthropogenic processes. Previous studies suggested that many trace elements which are mobilized in association with airborne particulates derived from high temperature combustion sources such as fossil fuel power plant, metallurgical smelter and blast furnace, municipal incinerator and automobiles. (52) Wiener (75) reported that increased concentrations of certain trace elements in soils around coal-fired power plants were detected. Burtine and Goldberg (7,9,32,37) reported that the total quantities of trace elements involving coal combustion were large, being roughly comparable to the quantities annually mobilized by the natural process of crustal rocks.

Chemically, the lignite is composed of several elements which are concentrated during decay period of reducing condition. The review of the literature indicated that the elements in coal could be divided into three groups. The first group consists mainly of major elements such as O, Si, Al, K, Ti, Mg, Ca, Na, Ba and Mn. The second group consists of Cl, Br, I, Mo, As, Sb, Sc, In, Hg, W, Ir, Au, Ag, Cu, Zn, Ni and Co. The third group contains elements with intermediate or irregular concentration ranges : Fe, V, Cr, Sc, Th, Hf and the rare earth elements. In coal, their behaviors are similar to that of the elements of the first group, whereas in ash, they occur as the elements of the second group. The elements of the first group occur largely or exclusively combined with oxygen as oxides, silicates, phosphates and carbonates as they formed the major constituents of the earth's crust (lithosphere). Their concentrations in coal ash are very close to the composition of crustal rock. The elements of the second group have different chemical properties from those of the first group. They form preferentially compounds free of oxygen such as sulfides, selenides, and antimonides. They are called sulfophilic elements, and can further be subdivided in chalcophilic and siderophilic elements. These rare

elements (second group) do not belong to the mineral fraction of coal, as they are enriched in coal and coal ash compared to the composition of crustal rock. The behavior of the elements of the third group can again be considered as intermediate between both fractions.

Klein et al^(9,32,52) had studied the behavior of the trace elements in coal fired power plant. Three classes of partitioning behavior were reported as the following.

Class 1, Al, Ba, Ca, Ce, Co, Eu, Fe, Hf, K, La, Mg, Mn, Rb, Sc, Si, Sm, Sr, Ta, Th and Ti showed little preferential partitioning between the bottom ash and the collected or discharged fly ash.

Class 2. As, Cd, Cu, Ga, Pb, Sb, Sc and Zn were quite concentrated in the fly ash comparing to the bottom ash, and were more concentrated in the fly ash which discharged through the stack than in that collected by the precipitator.

Class 3. Hg, Cl and Br remained essentially completely in the gas phase.

This classification correlated well with the reported of Natusch et al⁽⁵²⁾ and Kaakinen et al⁽³²⁾, who had studied the relationship between the trace element concentration and particle size in the fly ash. They reported that, all elements studied, Sb, As, Cd, Cr, Ni, Pb, Tl, Se and Zn showed a clear inverse relationship between concentration and particle size. Except for Cr, Ni, Zn and Cu (in the intermediate group), these elements are in Class 2. They reported no trend or poorly defined trends for Al, Ca, Co, Fe, K, Mg, Mn, Si, Ti, Rb and V. Of these elements V is in the intermediate group, but the other ten are in Class 1. A volatilization-condensation and absorption mechanisms were proposed by Natusch to account for the size-concentration behavior. Those elements which accumulate on the smaller fly ash particles were assumed to be volatile

at the temperature of combustion (1300-1600°C); as the flue gas cools, the volatiles condensed or adsorbed on the concentration of condensed elements should be inversely proportional to particle size. Those elements not volatile in the combustion zone from the fly ash particles upon which the volatiles condense. Natusch reported that the elements that were enriched on the smaller particles usually had boiling points comparable to or less than the temperature of the combustion zone. Thus, the small fly ashes which were highly enriched with many trace elements, could be transported considerable distance in the atmosphere before removed from the atmosphere by wet and dry deposition. (12,37,56) The trace elements which were discharged to the atmosphere could enter the terrestrial and aquatic environments, and atmospheric deposition of certain trace elements in natural system has increased considerably.

Klein⁽³⁷⁾ reported that the state of the trace elements in the coal is as in the following:

1. Trace elements in coal were present in aluminosilicates, as organic sulfides, or as organic complexes.
2. On combustion, the aluminosilicates were not decomposed. Rather, they melted and coalesced to create the bottom ash and fly ash.
3. During the initial stages of combustion, the conditions in a coal particles and with in its intermediate vicinity were probably reducing, and under these conditions the chemical bonding between metallic elements and sulfide mineral inclusions or between the elements and the organic matrix was broken, and these elements formed volatile species. If these elements were dispersed in the coal organic matrix, they became initially dispersed in the gas stream when the coal is burned.
4. The elements initially volatilized or dispersed in the flue gas steam may be condensed or absorbed on the fly ash as the temperature of the flue gas drops.

5. Since the bottom ash was in contact with the flue gas for a short time, and at high temperature, condensation of volatiles on the bottom ash was minimal.

2.2 Heavy metal in airborne particulates

Airborne particulates, especially in the area of coal combustion process are found to contain some heavy metals. Many heavy metals and/or their compounds are particularly toxic to human beings, animals and plants. Not much is known about their distribution in nature and their roles in air pollution. Heavy metals such as cadmium, copper, lead, manganese, nickel and zinc are currently concerned in this study.

2.2.1 Cadmium

Cadmium is a rare element in the earth's crust. Natural cadmium level in the atmosphere was estimated to be about $0.002 \mu\text{g}/\text{m}^3$. (10) The tendency of cadmium to be distributed in the atmosphere is partly due to its relatively high volatility, the melting point of the pure metal is only 765°C . (10) Health effects of this heavy metal include sterilization, high blood pressure, and cardiovascular disease which interferes with zinc and copper metabolism. (22,26) A disease specifically associated with cadmium poisoning had occurred in Japan as "itai-itai". (10,26,56) Chronic cadmium poisoning produced proteinuria and caused the formation of kidney stones. (10,26,56) Additionally, there were some evidence that cadmium was a carcinogen. (56) Inhalation of cadmium oxide fume, as occurred to certain occupations, led to severe pulmonary changes, including emphysema. An occupational exposure to $8 \mu\text{g}/\text{m}^3$ for 25 years caused cadmium poisoning. (26) Because of its high toxicity to men, animals and plants, it was important to be aware that the increase of cadmium level in the environment could present a significant health hazard.

2.2.2 Copper

Copper is one of the chalcophile elements which are found in sulfide deposits. Copper is often found as common air contaminants in forms of copper fume and salts. This heavy metal is an essential element in animal and plant nutrition. ⁽¹⁰⁾ Nevertheless, absorption of excess copper by man resulted in "Wilson's Disease" in which excess copper was deposited in the brain, skin, liver, pancreas and myocardium. ⁽¹⁰⁾

2.2.3 Lead

Lead is also a rare element in the lithosphere. The percentage of lead content of the earth's crust is between 10-15 ppm. ⁽¹²⁾ Natural level of lead in the atmosphere is about 0.0005 ug/m^3 . ⁽⁵⁶⁾ The U.K. Department of the Environment ⁽²⁴⁾ reported that a modern 2,000 MW power station, using high efficiency electrostatic precipitator and burning 5×10^6 tonnes y^{-1} of coal emitted only about 1 tonne y^{-1} of lead. The signs and symptoms of lead poisoning include abdominal pain, tenderness, constipation, headache, weakness, muscular aches and vomiting. ^(22,66) There is frequently a characteristic lead line on the gum margin. Chronic feeding of tolerable levels of lead induces tumours of the kidney subsequent to the renal degenerative changes. ⁽⁶³⁾

2.2.4 Manganese

Manganese is one of the essential elements. Introduction of manganese into the environment by human activity is not really a serious problem at present. Because of the high natural levels of this element in plants, animals and soils, it is difficult to increase them significantly by human industrial activities. Nevertheless, localized effects were found. Chronic poisoning occurred in the mining industry. Manganese in the atmosphere has adverse effects on human. Poisoning took the form of progressive deterioration in the central nervous system. ⁽¹⁰⁾

2.2.5 Nickel

Emission sources of nickel into the atmosphere are diesel oil, tobacco smoke, chemical, catalysts, steel and non-ferrous alloys.⁽²²⁾ A much greater sources of enviromental pollution are the consumptions of fossil fuels, which were reported to release 70,000 tonnes each year into the atmosphere.⁽¹⁰⁾ Urban air typically has 0.03 to 0.12 ug/m³ of nickel.⁽²⁴⁾ There are a fair amount of direct evidences that this element is carcinogen which leads to lung cancer.^(10,22,26,63) Additionally, it rapidly damages the respiratory system.⁽²⁶⁾

2.2.6 Zinc

Zinc is another chalcophile element which tends to be found in sulfide deposits along with cadmium, copper and lead. Like copper and manganese, it is an essential element in animal and plant nutrition.^(22,26) Nevertheless, consumption of excess zinc is toxic likely to the other essential elements. The symptom of zinc toxicity was iron-deficiency anema resulting from depression of iron-containing enzyme.⁽¹⁰⁾ Zinc is not inherently a toxic element. However its fume (zinc oxide), when inhaled fresh, caused a disease known as "brass founder's ague or brass chills".⁽⁶³⁾

2.3 Heavy metal in Mae Moh Project area

No report on the heavy metal contents in airborne particulates in the Mae Moh Project area was found. However an investigation of some heavy metals in the solid waste and lignite were carried out by the Institute of Environmental Research, Chulalongkorn University⁽³⁵⁾, and the results are shown in Table 1.

An investigation similar to the above was also carried out by Ecology and Environment Division, Public Communications Department, EGAT⁽¹⁸⁾ and the results are shown in Table 2.

Table 1. The content of heavy metals in solid waste and lignite at Mae Moh Project as found by Institute of Environmental Research, Chulalongkorn University. (35)

Type of Material	Concentration : $\mu\text{g/g}$			
	Cd	Ni	Cu	Pb
Lignite	Trace	515	15	Trace
Ash	Trace	35-610	10-51	Trace
Overburden	0.06-1.25	49-105	19-24	10-19.4

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Table 2 The content of heavy metals in solid waste and lignite at Mae Moh Project as found by EGAT. (18)

Type of Material	Concentration : $\mu\text{g/g}$				
	Cd	Ni	Cu	Pb	Cr
Lignite	0.5	11.3	4.8	5.0	6.0
Bottom ash	2.3	68.1	35.1	28.2	31.7
Fly ash	2.4	62.9	26.9	22.1	26.1

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From the above literatures, they indicated that the process of lignite combustion emitted and discharged the trace elements to the atmosphere as vapors and particles. Moreover, these particles have relatively greater concentrations of certain trace elements than the feed lignite and the collected fly ash. Likewise, it appears that the use of lignite-fired boiler for the generation of the electricity in the Mae Moh Basin will continue to rise in the future. Thus, the environmental impact and assessment of the trace elements in the area is necessary.



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