

## CHAPTER 2

### LITERATURE REVIEW

Coal, as a sedimentary rock, is a complex mixture of organic and inorganic matter, containing intimately mixed solid, liquid and gaseous phases, which have allothigenic and authigenic origins ( Vassilev *et al*, 2001). Oman *et al*, ( 2002) mentioned that, for coal fired power plant there are the important emissions of solid particles and gases into the atmosphere, the discharge of contaminated waters, chemicals, ash and slag, as well as the heat and materials from the processes. The problem is common to practically all coal-fired power plants in the world.

Review is conducted on literatures related to the waste water from coal fired power station, waste water treatment processes, chemicals used and metal removal technologies for some metals found in power plant waste water. Other heavy metal removal techniques were also reviewed.

#### **2.1 Wastewater Characteristic from Coal Fired Power Plant**

In a coal fired power plant source of pollutants in waste water comes primarily from the coal used in combustion process. Thus the characteristic of waste water generated in coal fired power plant will depend on the elements found in the type of coal fired. Other sources of pollutants are from corrosion products and chemicals used in the power plant.

Study by Vassilev *et al*, (2001) for Pernik subbituminous coal showed that waste water generated from use of low grade coal(LGC) had pH 4.1–6.3 (acid to slightly acid), whereas the amount of the resulted dry water soluble residue (DWSR) is 0.3–1.2% (salty total mineralization). The chemical composition of DWSR are shown in Table 2.1.

Table 2.1 – Chemical composition for dry water soluble residue of Pernik subbituminous coal.( Vassilev *et al*, 2001 )

<b>Element Category</b>	<b>Element</b>	<b>Concentration</b>
Major Elements	Calcium	13.4 – 15.8 %
	Sulphur	15.7 %
	Magnesium	6.3 – 7.2 %
	Sodium	4.6 – 6.6 %
	Potassium	0.9 – 1.7 %
	Iron	1.4 %
Minor Elements	Silicon	0.9 %
	Aluminium	0.4 %
	Chloride	0.1 %
Trace Elements	Manganese	150 – 524 ppm
	Copper	88 – 141 ppm
	Zinc	115 – 121 ppm
	Lithium	68 ppm
	Nickel	62 ppm
	Cobalt	44 ppm
	Rubium	26 ppm
	Bromine	24 ppm
	Lead	9 – 19 ppm

Table 2.2 – Chemical composition for water-extractable portions of low grade coal  
(Vassilev *et al*, 2001 )

<b>Element</b>	<b>Concentration</b>
Chloride	24 %
Sulphur	13 %
Copper	0.4 – 3.8 %
Zinc	0.5 – 2.4 %
Manganese	0.5 – 2.0 %
Lead	0.1 – 1.5 %
Cobalt	0.9 %
Nickel	0.8 %
Lithium	0.6 %
Rubium	0.1 %

The chemical composition of water-extractable portions of LGC is shown in Table 2.2. Vassilev *et al*, (2001) mentioned that this leaching indicates that substantial Cl and S parts in LGC are related to the presence of water-soluble salts and organic materials. In contrast, the behaviour for Br, Co, Cu, Li, Mn, Ni, Pb, Rb, and Zn can be explained by their occurrence in strongly bound organic and inorganic water-insoluble forms.

In the Netherlands, the behavior of Hg in coal-fired power plants has been studied extensively. On average, the fate of Hg entering the power station in the coal was as follows: <1% in the bottom ash, 49% in the pulverized fuel ash (ash collected in the ESP), 16.6% in the FGD gypsum, 9% in the sludge of the wastewater treatment plant, 0.04% in the effluent of the wastewater treatment plant, 0.07% in fly dust (leaving the

stack), and 25% as gaseous Hg in the flue gases and emitted into the air ( Meij *et al*, 2002 ).

## **2.2 Waste Water Treatment For Coal Fired Power Plant**

During operational phase, the total volume of waste water has been estimated to be 62 L/hr. (1500 L/day). The raw wastewater from the power station contain heavy metals. The possible impacts normally are bioaccumulation of metal in fish and shellfish in the area. Like metals, the raw wastewater from the power station contain oxygen demand substances and suspended and dissolved solids. Data from the Kapar Power Power Station indicates that the total BOD load may reach up to 4.8 kg/day. This level can be considered to pose insignificant impact. To prevent possible contamination, the waste water will be treated at the power station waste treatment plant before discharged to the marine systems ( DEIA,1997).

### **2.2.1 Chemical Processes for Wastewater Treatment**

According to EPA (2007), chemical precipitation is used for the removal of metal compounds from wastewater. In the chemical precipitation process, soluble metallic ions and certain anions are converted to insoluble forms, which precipitate from the solution. Most metals are relatively insoluble as hydroxides, sulfides, or carbonates. Coagulation processes are used in conjunction with precipitation in order to facilitate removal by agglomeration of suspended and colloidal materials . The precipitated metals are subsequently removed from the wastewater stream by liquid filtration or

clarification (or some other form of gravity assisted sedimentation). Other treatment processes such as equalization, chemical oxidation or reduction (e.g., hexavalent chromium reduction), precede the chemical precipitation process. The performance of the chemical precipitation process is affected by chemical interactions, temperature, pH, solubility of waste contaminants, and mixing effects.

### **2.2.2 Chemicals Used in Precipitation**

EPA (2007) mentions that chemicals, such as sodium hydroxide or lime, are frequently used in order to raise the pH of the wastewater to a range somewhere between 9 to 12 in order to optimize precipitation of metal compounds. Precipitation using sodium hydroxide or lime is the conventional method of removing metals from wastewater. However, sulfide precipitation is also frequently used instead of hydroxide precipitation in order to remove certain metal ions. Hydroxide precipitation is effective in removing such metals as antimony, arsenic, chromium, copper, lead, mercury, nickel, and zinc. Sulfide precipitation is more appropriate for removing mercury, lead, and silver. Carbonate precipitation, while not frequently used is another method of chemical precipitation and is used primarily to remove antimony and lead.

Paternstorm( 2007) described that zinc and lead containing wastes may be classified as hazardous wastes, and must pass the toxicity characteristic leaching protocol (TCLP) test mandated by the EPA. The TCLP test requires that lead (the constituent

of concern) levels be below a prescribed 5 ppm level. In order to meet this test, it was found that a 4-8% by weight lime addition would precipitate sufficient lead and also zinc to meet the applicable level. Use of lime of in waste water treatment has the advantage to bind the heavy metals in the sludge and reduce their leacheability. This method is extremely beneficial in reducing zinc and lead quantities in a wastewater stream, and also resulting slurry passes the TCLP test and is considered nonhazardous.

### **2.2.3 Other Useful Applications of Lime**

Lim *et al*, 2002 described lime as a commonly used chemical for wastewater treatment, soil treatment and other processes in many industries. Lime has been widely used to improve the properties of clay soils, since the Roman times. Lime reacts with water contained within the clay, and thereby releases calcium cation (Ca(II)) and hydroxyl anions (OH<sup>-</sup>) in solution. The calcium-saturated solution surrounding the clay mineral particles results in cation substitution and particle flocculation and agglomeration, thereby modifying the clay . Under conditions of a high pH, slower and longer-term stabilization reactions occur, resulting in gel formation and subsequent crystallization.

The emission of SO<sub>2</sub> from the coal combustion is commercially suppressed principally by flue gas scrubbers; however, the high cost discourages their installation in some old combustion plants. Sorbent injection technology using calcium-based

sorbents such as limestone and hydrated lime is relatively low in capital cost and can easily be retrofitted so that it provides an alternative process for controlling SO<sub>2</sub> emission. However, low sorbent utilization efficiency is a major drawback of this technology. About 50% of SO<sub>2</sub> removal efficiency usually requires Ca/S ratio of 2–4 when limestone is employed (Fan *et al*, 2003).

The addition of lime, fly ash, and loess into the water/wastewater sludge decreased the water content of the original sludge, which was in fact one of the major problems in recycling sludge. Especially, the use of fly ash showed a significant effect, but the large amounts of fly ash, more than 200%, resulted in a negative effect. As the amount of the modifiers in the sludge increased, the optimum moisture content decreased and the dry density increased (Lim *et al*, 2002) . For information loess is a homogeneous, typically nonstratified, porous, friable, slightly coherent, often calcareous, fine-grained, silty, pale yellow or buff, windblown sediment (Wikipedia, 2008)

#### **2.2.4 Proprietary Chemicals Used in Chemical Precipitation**

Mcilvaine company (2006) mentions the use of proprietary chemical TMT 15 ( trimercapto-S-triazine) in both the scrubber slurry and wastewater treatment for mercury removal . At higher pH it also effectively precipitates Cu, Zn, Ni, Cd and other heavy metals . Estimated usage in wastewater treatment is 2-10 ml TMT 15/ton of coal and it can also be used to prevent mercury re-emission in the scrubber but this requires 10-50 ml TMT 15/ton of coal.

Use of Nalmet , a proprietary chemical developed by NALCO, has been reported by Mcilvaine company (2006) for 50 to 80 percent removal of selenium. It also reported that a plant with discharge violation for mercury levels 2-3 times allowable utilized Nalmet to meet compliance for three years.

### **2.3 Coagulation**

The coagulation process is not always perfect and may result in small flocs when coagulation takes place at too low temperature or fragile flocs which break up when subjected to physical forces (Hanson and Cleasby, 1990a and 1990b). It is important to improve the coagulation and flocculation processes to obtain a good quality effluent and the rapid sedimentation of the flocs. Use of polyelectrolyte can help to improve floc size and settling time.

In conventional wastewater treatment systems, coagulants such as aluminum chloride, ferrous sulphate, aluminum sulphate, ferric chloride and hydrated lime are the most widely used because of their effectiveness, cheap, easy to handle and availability (Edzwald ,1993).

Among the available coagulants, aluminum sulphate (alum) and poly-aluminum chloride (PAC) are the most extensively used coagulant for sludge conditioning and dewatering coagulation processes (Al-Mutairi *et al*, 2004 and Kevin *et al*, 2004). The most commonly used are the aluminium coagulant ( Ahmad *et al*, 2006). They are more effective at lower temperatures, a broader pH range and forms positive charged



Al species that adsorb to negatively charged natural particles resulting in charge neutralization (Zhao, 2003). These coagulants could cause hazardous activated sludge which contains residual aluminum which may cause side effects when discharged into the open water course (Pontius, 2000) . It has been pointed out that intake of large amount of aluminum salt may cause Alzheimer's disease (Pontius, 2000).

### 2.3.1 Effects of Polymer on settling rate of sludge.

Bache and Zhao (2001) have demonstrated that the viscosity of the supernatant of a polymer-dosed sludge changed with the polymer dosage. Zhao (2003) has tested the viscosity supernatant of polymer-dosed sludge samples by withdrawing immediately after 30 min settlement and its viscosity was measured by using an Ostwald Calibrated Viscometer at  $20\pm 1$  °C. The plot shown in Figure 2.1 illustrates the pattern of viscosity from decrease to increase with the increase of polymer dose.

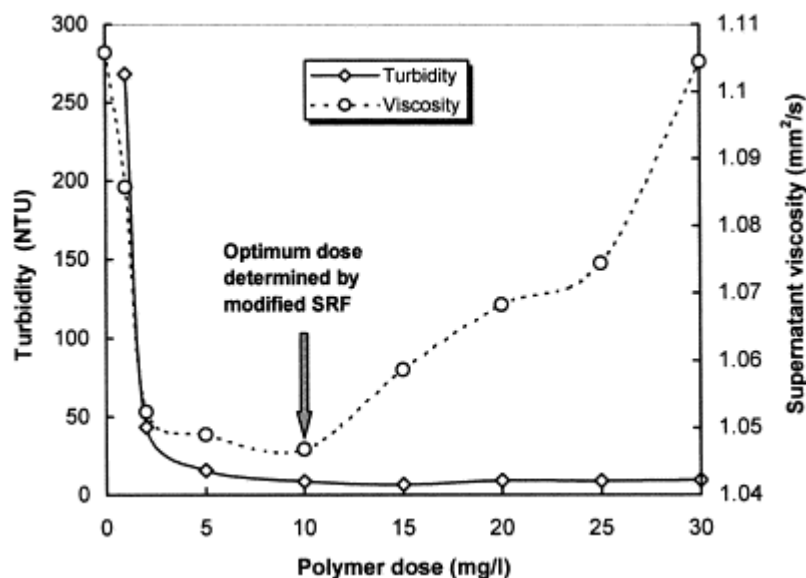


Figure 2.1 Pattern of supernatant viscosity and turbidity with the polymer dosage (SS=4.595 mg/l). Samples were withdrawn at 30 min settling.

( Zhao, 2003)

The direct effect of viscosity on settling time of the sludge was also studied by Zhao (2003 ). Plot shown in Figure 2.2 shows the relationship.

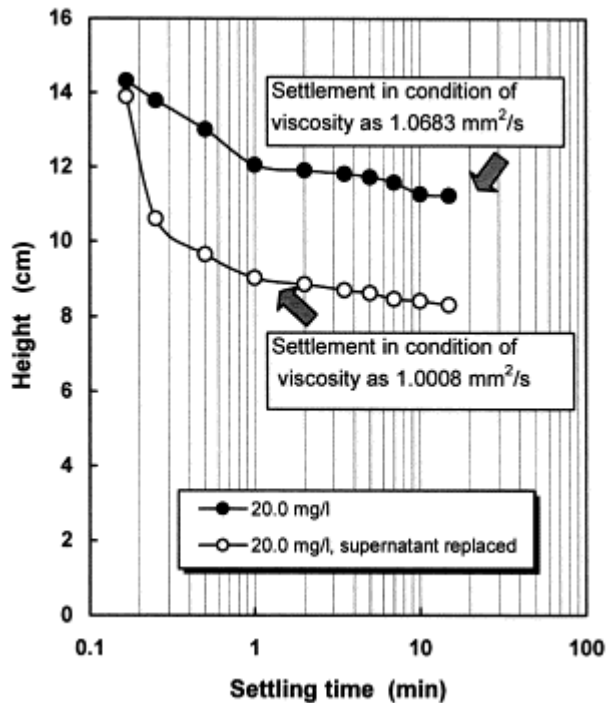


Figure 2.2. Effect of supernatant viscosity to the settling behaviour (predosed at 20.0 mg/l with polymer, using 100 ml measuring cylinder, SS=4.595 mg/l).

( Zhao, 2003)

Zhao (2003) states that there are many unresolved difficulties and problems in trying to integrate the phenomena which control the settling behaviour. It is believed that the settling behaviour of flocculated suspension is complex, depending on factors such as floc size, density, velocity, viscosity, flocculation and wall effect as well as the formation of aggregate structures.

## **2.4 Other Heavy Metal Removal Techniques**

Other than precipitation and flocculation other techniques of heavy metal removal like ion floatation and adsorption is possible. Natural materials that form complexes with metal ions using their ligand or functional groups can be used as absorbent. Processes for metal removal like adsorption have been suggested as being cheaper and more effective than the other technologies (Gabaldon *et al*, 1996).

Flotation processes have been widely and successfully used for mineral treatment. Recently, these processes have also been employed as an alternative strategy for wastewater treatment. Unlike other technologies, flotation processes can be successfully applied to systems where differences between the density of the continuous phase and of the particulate phase are small, classic examples are flocculent emulsions and suspensions ( Puget *et al*, 2004 ).

### **2.4.1 Heavy Metal Removal using Flotation of Ions**

Polat and Erdogan (2007) have studied the use of ion flotation to remove heavy metals in waste waters. Tests were conducted using synthetic waste water prepared by using known concentration of Cu(II), Zn(II), Cr(III) and Ag(I). Various parameters such as airflow rate, surfactant and frother concentrations and water chemistry were tested to determine the optimum flotation conditions. Anionic sodium dodecyl sulfate

(SDS) and cationic hexadecyltrimethyl ammonium bromide (HTAB) were used as collectors. Ethanol and methyl isobutyl carbinol (MIBC) were used as frothers. Metal removal reached about 74% under optimum conditions at low pH. At basic pH it became as high as 90%, probably due to the contribution from the flotation of metal precipitates.

It was observed that it was possible to find conditions to concentrate these metals with recoveries as high as 90% in a froth phase which contain less than about 20% of the original water. Considering the ease of application, low cost and very high capacities achievable in the flotation process, such results are very promising (Polat and Erdogan, 2007).

Selective floatation of copper from zinc and silver ions was also studied by Polat and Erdogan (2007). For copper–zinc system, the best separation between the two was observed at pH 4 where both metals must be present in their cationic forms. The fact that copper floats much more readily at this pH compared to the similarly charged zinc species is an indication of a higher affinity of the copper species towards the SDS molecules.

#### **2.4.2 Heavy metal removal by Absorption Method**

Pehlivan *et al.*, (2006) has conducted study on heavy metal removal using sugar beet pulp (SBP) and fly ash (FA). Heavy metals used in the test were zinc and copper. Both SBP and FA showed capability to remove heavy metal by absorption. SBP is composed mainly of cellulose (20–30%), pectin (26–40%), pentozan(24%),

protein(5%), and lignin (10%), all of them with the capacity to bind metal cations due to carboxylic and phenolic groups. The metal ions are mainly fixed on these acid sites. At pH values higher than 3–4, carboxyl groups are deprotonated and negatively charged. Consequently, the attraction of positively charged metal ions would be enhanced. At low pH, the surface of SBP would also be surrounded by hydronium ions which decrease the metal ion interaction with binding sites of the sorbent by greater repulsive forces. The smaller sorption values observed at pH values 3.0–4.0 have been attributed to the competition between the sodium ion and the metal ions released. As expected, the sorption increases with pH. As the pH increased, the overall surface on the SBP became negative and the metal sorption is improved due to the lower competition between the sodium ions and metal ions. The plot in Figure 2.3 shows the removal percentage of zinc and copper.

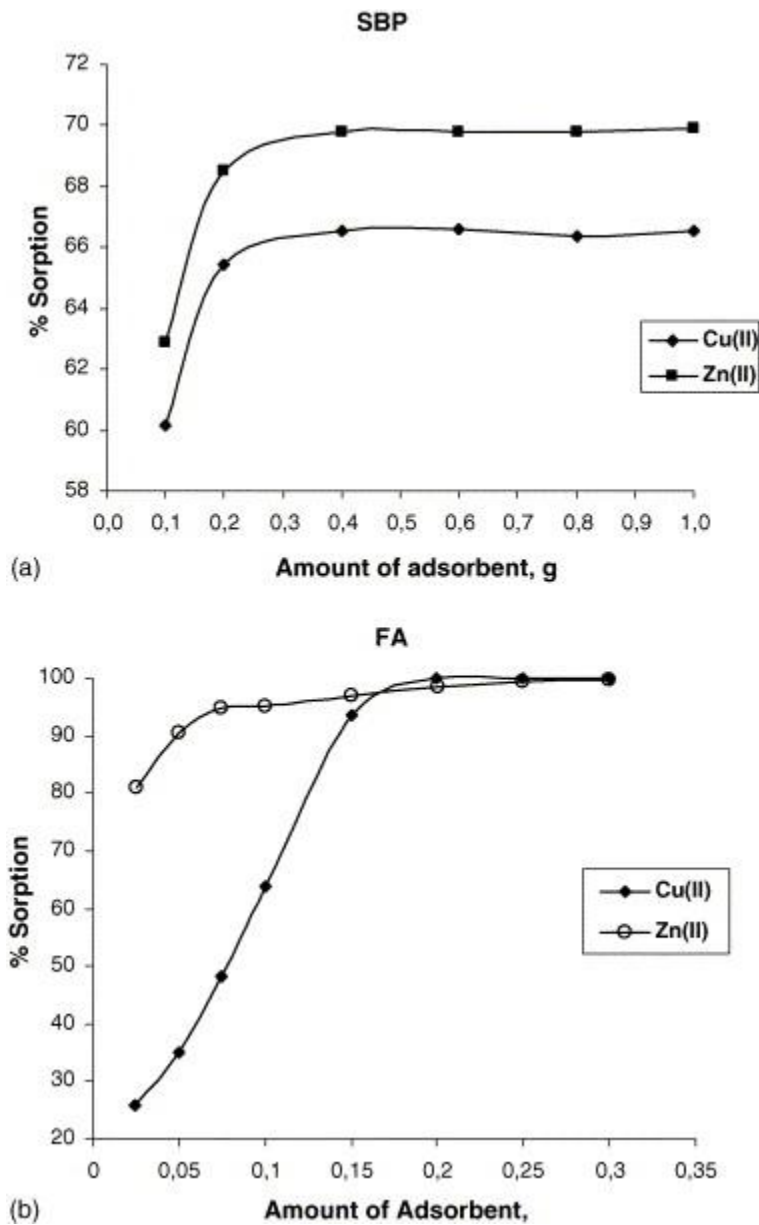


Figure 2.3 Effect of amount of adsorbent on the sorption of copper and zinc by sugar beet pulp (SBP). (b) Effect of amount of adsorbent on the sorption of copper and zinc by fly ash (FA).

(Pehlivan *et al*, 2006 )

For FA, Pehlivan *et al.*(2006) explains that it contains abundant alkaline materials, such as CaO and MgO, and the hydroxide ion (OH) is liberated, raising pH during adsorption. In such cases, Cu(II) may then form an insoluble product of  $\text{Cu(OH)}_2(\text{s})$ . The Zn and Cu removal capacity exhibited by the FA depends on the pH of the initial

metal solution, decreasing with decreasing pH. The maximum adsorption of copper and zinc was found to occur at pH 4.0–8.0. This may be attributed to the surface charge development of FA and the concentration distribution of metal ions which both are pH-dependent. All experiments were carried out in the pH range of 2.0–8.0 where chemical precipitation is avoided, so that metal removal could be related to the adsorption process. It was evident that the maximum uptake of copper and zinc occurred at pH 5.5 and 6.0, respectively, for SBP and at pH 5.0 and 4.0, respectively, for FA. The pH of the solution was measured before and after the adsorption with SBF and slightly change was noticed in the pH. Due to the alkaline nature of FA, the pH increases as the FA is added into the solution. When the above occurs, the copper and zinc ions are expected to precipitate out of the solution under higher pH conditions. To elucidate the effect of such a pH increase on copper and zinc removal with FA, experiments were performed with pH control.

Katsou *et al* (2011) examined the adoption of a sorbent-assisted ultrafiltration (UF) system for the reduction of Pb(II), Cu(II), Zn(II) and Ni(II) from industrial wastewater. In such a system metals were removed via several processes which included precipitation through the formation of hydroxides, formation of precipitates/complexes among the metal ions and the wastewater compounds, adsorption of metals onto minerals (bentonite, zeolite, vermiculite) and retention of insoluble metal species by the UF membranes.

At pH = 6 the metal removal sequence obtained by the UF system was Pb(II) > Cu(II) > Zn(II) > Ni(II) in mg g<sup>-1</sup> with significant amount of lead and copper being removed

due to chemical precipitation and formation of precipitates/complexes with wastewater compounds. At this pH, zinc and nickel adsorption onto minerals was significant, particularly when bentonite and vermiculite were employed as adsorbents. Metal adsorption onto zeolite and bentonite followed the sequence  $Zn(II) > Ni(II) > Cu(II) > Pb(II)$ , while for vermiculite the sequence was  $Ni(II) > Zn(II) > Cu(II) > Pb(II)$  in  $mg\ g^{-1}$ . The low amount of  $Pb(II)$  and  $Cu(II)$  adsorbed by minerals was attributed to the low available lead and copper concentration. At  $pH = 9$  the adoption of UF could effectively reduce heavy metals to very low levels. The same was observed at  $pH = 8$ , provided that minerals were added. The prevailing metal removal process was the formation of precipitates/complexes with wastewater compounds ( Katsou *et al*, 2011 ).

## **2.5 Heavy Metal Removal Process**

### **2.5.1 Chromium Removal Process**

Chromium is a heavy metal of commercial importance, thus significant amounts are released in wastewaters. Chromium in wastewaters and in the aquatic environment is primarily encountered in oxidation stages +3 ( $Cr^{(III)}$ ) and +6 ( $Cr^{(VI)}$ ). Recent publications suggest that  $Cr^{(VI)}$  compounds are more toxic than  $Cr^{(III)}$  ones, while  $Cr^{(III)}$  has been identified as trace element, at least for complex organisms ( Vaiopoulou and Gikas, 2012 ).



Chromium occurs naturally as chromite, ( $\text{FeCr}_2\text{O}_4$ ) (Bartlett, 1997). Chromium occurs in aqueous system as both the trivalent (Cr (III) ) and the hexavalent (Cr (VI) ) ions (Patterson, 1975) . Chromium(III) and chromium(VI) are interchangeable in the natural environment, depending on the pH and redox potential of the medium and the presence or absence of a strong oxidant or reductant. In the presence of ferrous iron, organic matter and sulphides, chromium(VI) can be biologically reduced to chromium(III)(Rai *et al*, 1989). The Cr (VI)/Cr (III) half reaction has such a high redox potential that there are few oxidants present in natural systems capable of oxidizing Cr(III) to Cr(VI). The most likely strong oxidants that can oxidize Cr(III) to Cr(VI) are  $\text{O}_2$  and  $\text{MnO}_2$ , although oxidation by oxygen is generally slow (Bartlett, 1997).

Patterson, 1975 also mentioned that reduction of hexavalent chromium from a valence state of plus six to plus three, and subsequent hydroxide precipitation of the trivalent chromic ion, is the most common method of hexavalent chromium control. Sulfur dioxide is the most popular reducing agent used in treatment of chromium wastes, primarily because it is relatively inexpensive (Stone, 1972). In one full-scale application to treat chromium in a metal-finishing waste, the wastewater is adjusted to pH 2.5 with sulfuric acid before reduction (Halse *et al*, 1960) . An unusual source of sulfur dioxide has been reported in use at one plant to treat hexavalent chromium in plating wastes . Sulfur dioxide is washed out of the powerhouse stack gas and used as the chemical reducing agent for converting hexavalent chromium to the trivalent form (Fisco, 1970). Use of sulfur dioxide for reduction imparts an oxygen demand to the waste effluent, unless the effluent is oxygenated by passing air through it (Lacy and Cywin, 1968) .

Patterson (1975) mentioned that two stage chromate reduction has been used at several plants . In the first stage sulfur dioxide, sodium bisulfite or metabisulfite is employed. This is followed by a second “polishing” stage of chromate reduction with hydrazine .

Several installations employ ferrous sulfate as a reducing agent for chromate (Patterson, 1975) . Ferrous sulfate has been reported to have the advantage of effectiveness independent of pH (Germain *et al*, 1968). However, Bennett (1973) claims that ferrous sulfate reduction at pH 2-3 proceeds within 30 minutes to a residual hexavalent chromium level of 1 mg/l, but at pH above 4, equivalent treatment requires one hour. It has also been reported that use of ferrous sulfate yields much greater sludge than are produced through use of sulfur dioxide or bisulfite, since voluminous iron precipitates will simultaneously form in the chromic precipitation step (Bennett, 1972 and Besseliver, 1996) . Patterson (1975) indicated that use of ferrous sulfate to treat chromate wastes containing cyanide results in the formation of very stable complexes, which will prevent subsequent effective cyanide treatment.

Trivalent chromium can be removed as insoluble hydroxide ,  $(Cr(OH)_3$ , by precipitation with caustic soda or lime (Besseliver, 1996 ).

Use of ferrous sulfate as the hexavalent chromium-reducing agent preparatory to trivalent chromium precipitation will produce four times the sludge weight encountered with use of other reductants upon precipitation of the chromium hydroxide (Kraljik, 1975) . The specific choice of base for pH adjustment will also influence the sludge production with lime yielding roughly three times more sludge

compared to soda ash ( $\text{Na}_2\text{CO}_3$ ) or caustic soda ( $\text{NaOH}$ ), due to formation of calcium carbonate or sulfate (Patterson, 1975) .

### **2.5.2 Copper Removal Process**

As with most heavy metal wastes, treatment process employed for reduction of soluble copper in wastewaters may involve precipitation and disposal of resulting sludge solids, or recovery process such as ion exchange, evaporative and electrolysis (Patterson, 1975). Ion exchange is an appropriate treatment method for wastewaters containing copper less than 200 mg/l ; precipitation is applicable for copper levels of 1.0 – 1,000 mg/l, and electrolytic recovery is advantageous for treatment at wastewater copper concentrations above 10,000 mg/l (Dean *et al*, 1972) .

Standard treatment methods for copper and most heavy metals is precipitation as the relative insoluble hydroxide, at alkaline pH, or occasionally as the sulfide (Patterson, 1975) .

Coprecipitation by addition of ferrous sulfate has also been suggested for strongly complexed copper wastewaters such as originate from electroless plating baths and rinses (Wing *et al*, 1977a) and (Wing and Rayford, 1977) . The process is somewhat complicated, requiring pH adjustment in two steps to break the copper to the cuprous form to prevent recomplexation (Wing *et al*, 1977b) . Lime is usually preferred to the more expensive sodium hydroxide and in the presence of high sulfate, considerable calcium sulfate precipitate may form (Patterson, 1975).

Copper cyanide-complexed wastewaters can be treated by first destroying the cyanide, followed by conventional copper treatment (Wagner, 1972). Typically, cyanide destruction is by alkaline chlorination process and excess chlorine may be required in the presence of copper or other metal ions which catalyze the spontaneous destruction of hypochlorite (Patterson, 1975) .

### **2.5.3 Manganese Removal Process**

The industrial sources of manganese are steel alloy, dry cell battery, glass and ceramic, paint, ink, dye and fertilizers (Patterson, 1978). It also occurs in metal mines, mine drainage, especially in coal fields. The highly soluble manganous chloride is used in dyeing operation, linseed oil dryers, and electric batteries, while the equally soluble manganous sulfate is used in porcelain glazing, varnishes and production of fertilizers (Patterson, 1975).

Due to the low reactivity of manganous ion with oxygen, simple aeration is not effective oxidation technique below pH 9.0 and even above that pH the reaction is slow (Welch, 1963) .

The use of chemical oxidants to convert manganous ion to insoluble manganese dioxide, in conjunction with coagulation and filtration, has been recommended (Patterson, 1975). Generally mechanical or natural aeration devices are employed , primarily for iron oxidation and manganese removal is also accomplished even though pH is not optimal for manganese oxidation (Patterson, 1975) . The successful

use of potassium permanganate as a chemical oxidant has been reported (Patterson, 1975) . Addition of 1.5 – 2.0 mg/l potassium permanganate reduced 1.0 mg/l manganese to less than 0.05 mg/l (Haney, 1964). The absence of residual taste or odor has been cited as an additional advantage of permanganate use over chlorination in water supply application (Borgren, 1963) .

The character of manganese flocs produced when strong oxidants are used has been reported to rapidly clog slow sand filters (Borgren, 1963). Effective manganese oxidation by chlorination requires a free residual of 0.5 mg/l, and a dosage of 1.29 mg chlorine/mg manganese oxidized (Harris, 1962).

Ion exchange process has also been utilized for iron and manganese removal (Patterson, 1975). The advantages cited include smaller capital investment than coagulation-filtration , nearly four times greater flow rates, smaller plant requirements, and simple operation (Alzentzer, 1963). The obvious drawback to ion exchange is the nonselective removal of other ions which increases operation cost (Patterson, 1975).

#### **2.5.4 Zinc Removal Process**

Industries discharging waste streams which contain significant levels of zinc include steel works with galvanizing lines, zinc and brass metal works, zinc and brass plating, viscose rayon yarn and fiber production, groundwood pulp production and newsprint paper production (Patterson, 1975).

Treatment process employed for wastewater zinc removal may involve either chemical precipitation, with disposal of the resultant sludge, or recovery. Recovery may involve ion exchange, evaporative recovery and other processes including precipitation (Patterson, 1975). The precipitation process most frequently employed involves adjustment of pH with either lime or caustic to achieve alkaline conditions, and precipitation of zinc hydroxide .

Theoretical considerations and laboratory studies on pure zinc solutions indicate optimum treatment pH of 9.0 – 9.8 (Yost and Scarfi, 1978, and Yost and Scarfi, 1979) . Yost and Scarfi (1978) have reported optimum zinc precipitation treatment at pH 11 and above for zinc-plating rinses containing alkaline cleaning compounds.

## **2.6 Chemical Oxygen Demand (COD) and Nutrient Removal**

Adsorption as a wastewater treatment process has aroused considerable interest during recent years. Commercial activated carbon is regarded as the most effective material for controlling the organic load ( Aluyor and Badmus, 2008 )

It was found that activated animal horn carbon (AHC) competed favourably with commercial activated carbon (CAC). The results obtained showed that AHC can be used in the removal of COD from industrial wastewaters. Trend of COD removal by AHC, 95.67%, is comparable to that of CAC with 96.34% efficiency. These results show that granular activated carbons made from agricultural waste (animal horn) can

be used with greater effectiveness for organic matter removal from industrial wastewater ( Aluyor and Badmus, 2008 ).

Bioaugmentation was often applied to enhance the nutrients removal in conventional processes in China ( Yong *et al*, 2010). The bioaugment process, which installed polyurethane foams as carriers and inoculated specialized bacteria on the media, was found more easily started up in lower DO concentrations ( Guo *et al*, 2009). Zeolite was also used to enhance conventional contact stabilization activated sludge process and improved nitrogen removal for 27%, by the mechanism of preferential ion exchange of zeolite to ammonium ( Wu *et al*, 2008 ).

Textile effluents are among the most difficult industrial wastewaters to treat because of their compositional variability and of the presence of numerous different chemicals intentionally designed to resist degradation. Ozone integration in a sequencing batch biofilter granular reactor was tested at laboratory scale for treating a printing wastewater characterized by high concentrations of surfactants and nitrogen. The process was optimized in terms of applied organic load and ozone dose ( Lotito *et al*, 2012 ).

## **2.7 System for Chemical Management in Wastewater Treatment Plants**

In January 2002, Zero Waste Alliance and the City of Portland completed a plan for managing and systematically reducing chemical use at the city's wastewater treatment facility. The plan, called Enhanced Chemical Management System(ECMS), provides a structured way to manage the dangers of chemicals use at the facility.

Portland's wastewater treatment plant now possesses an enhanced chemical management system that identifies chemicals of concern and guides its employees in the goal of continual reduction of hazards and costs. Using the ECMS reduced chemical management costs by \$ 100,000. It reduced reporting requirements by \$ 50,000 and lowered the costs of safety management by \$ 25,000. The total annual savings is estimated to be \$ 190,000. Because these reductions of cost and exposure potential are research-based, systematic , and well documented, the reductions have no negative impacts on the efficiency or effectiveness of wastewater treatment at the plant. The system is continually updated and contains correction and auditing provisions so that good ideas are recognized and made into policy, and so that policies change as circumstances change ( Portland, 2010).

Normally, in some of the developing countries wastewater treatment alternatives are evaluated only based on economic criterion (Guangming *et al.*, 2007). The analytical hierarchy process (AHP) is a systematic technique for multi-criteria decision-making that facilitates an abstruse definition of premiership and precedence of decision makers (Saaty, 1980).

Study on Tehran province electroplating plants and has been done during 2007 year. The best wastewater treatment alternative was selected by AHP. Experts' knowledge was integrated by weighing criteria and indices. Four treatment alternatives include reverse osmosis, nano filtration, ion exchange and chemical precipitation were studied. The results showed the best alternative for 1 m<sup>3</sup>/d and 5 m<sup>3</sup>/d flow rates were chemical precipitation and reverse osmosis with 0.33 and 0.31 scores, respectively ( Dabaghian *et al.*, 2008 )



## 2.8 Design and Configuration of Sultan Azlan Shah Power Station

Sultan Azlan Shah power station is built on a man made island which consists of 34 hectares for Lekir Bulk Terminal (LBT), 189 hectares for the 25 years ash pond and 102 hectares for the power plant and coal stockyard. Figure 2.4 shows the location of the various parcels.

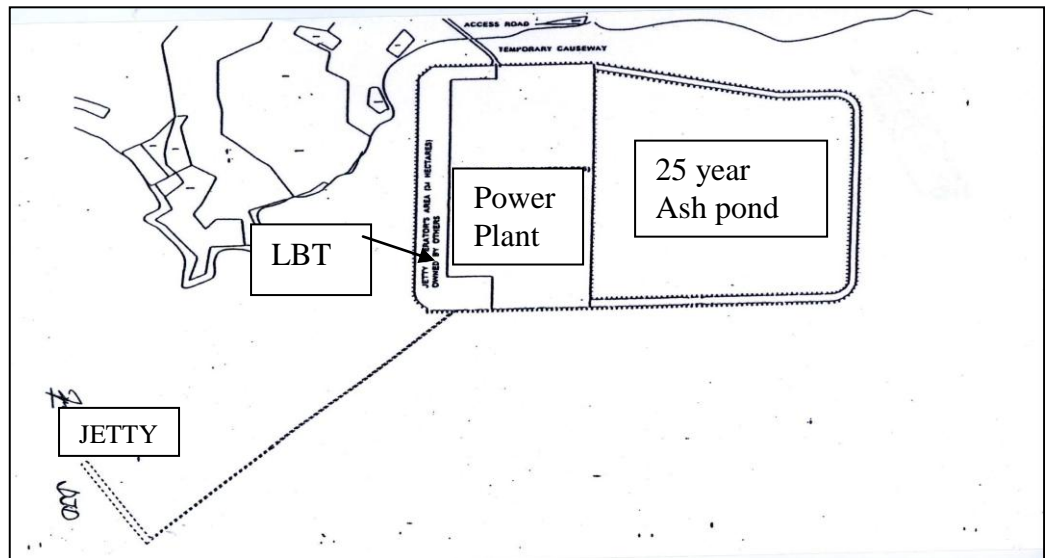


Figure 2.4 : Diagram showing man-made island and various parcels of Sultan Azlan Shah Power Station

Source : TNBJ 2007

The generating units' configuration is 3 x 700 MW (nett). The boilers use sub-bituminous coal as main fuel. Sources of coal used are mainly from Kalimantan (Indonesia ) and Newcastle ( Australia). The common brands of coal used in the power station are :

- a) ADARO

- b) LATI
- c) MELAWAN
- d) HUNTER VALLEY
- e) ROTO SOUTH
- f) SATUI

Different brands of coal have different values of calorific value(CV), volatile matter, ash content and moisture content. The combustion settings have to be varied for the different types of coals in order to optimise the combustion process. The main components of the power station consists of :-

- a) Boilers
- b) Steam Turbines and Generators
- c) Main Fuel System
- d) Cooling Water System
- e) Raw / Demineralised Water System
- f) Flue Gas System - Electrostatic Precipitators
  - Desulphurisation Plant
  - Chimney
- g) Electrical Systems

The plant layout is such that it can operate as independent units with certain common auxiliaries being shared. The boilers produce steam with a pressure of about 180 bars and the steam is introduced into steam turbines which are coupled to generators. The generators produce electricity, which is stepped up to 500 kV and distributed via the grid system.

Right from the inception of the project emphasis has been made on environmental requirements. The plant has been designed to meet emission limits in Table 2.3. These emission limits were adopted based on best available technology at that time and were more stringent than existing regulations.

Table 2.3 - Design Emission Limits

<b>Parameter</b>	<b>Design Emission Limit</b>
Sulphur Dioxide (SO <sub>2</sub> )	750 mg/Nm <sup>3</sup> maximum
Nitrogen Oxide (NO <sub>2</sub> )	650 mg/Nm <sup>3</sup>
Particulates/ Dust	50 mg/Nm <sup>3</sup>
Opacity	20%
CO	200 mg/Nm <sup>3</sup>

The plant uses clean coal technology and the environmental control equipments and processes installed to minimise pollution are :

- a) Combustion Process – utilisation of low NOx burners
- b) Electrostatic Precipitators
- c) Flue Gas Desulphurisation Plant
- d) Continuous Emission Monitoring System
- e) Ambient Air Quality Monitoring Stations
- f) Main Wastewater Treatment Plant
- g) Coal Yard Wastewater Treatment Plant
- h) 200m high Chimney
- i) 25 years Ash Pond.

Electricity generation process flow is shown in figure 2.5 while the side elevation of the generation plant is shown in Figure 2.6.

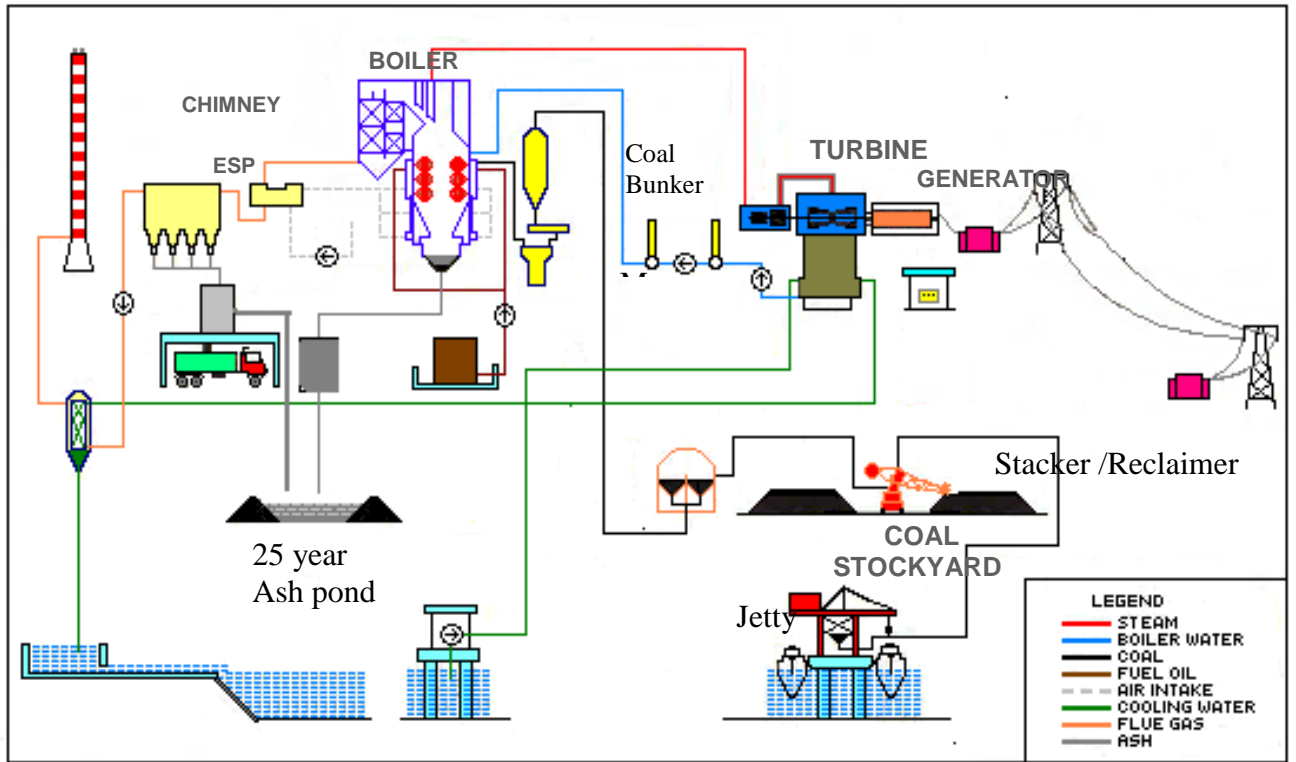


Figure 2.5 –Electricity Generation Process Flow

Source : TNBJ ( 2007 )

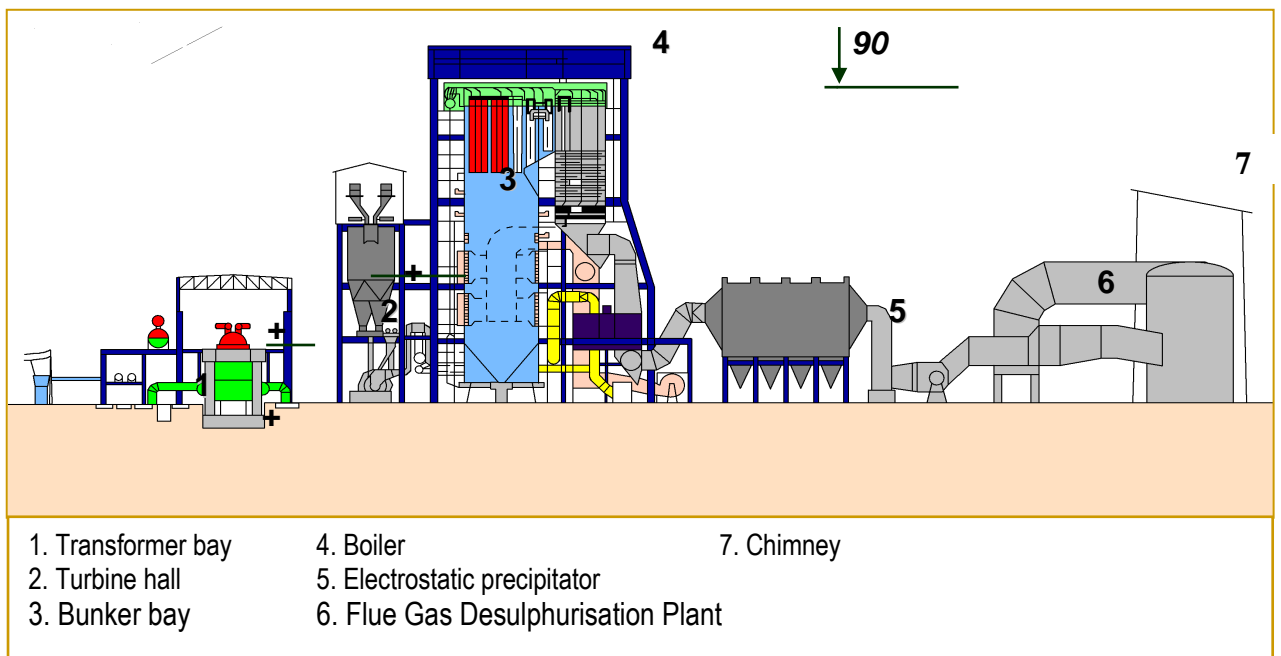


Figure 2.6 – Side Elevation of Electricity Generation Plant

Source : TNBJ ( 2007 )