A review on the existence of chrome in cement and environmental remedies to control its effects

S. Bodaghpour[a], N. Biglari Joo[b], S. Ahmadi[b]

Abstract**—** Due to different factors in cement production such as raw materials, fuels and additions many of heavy metals have the chance to enter the clinker and final cement product. In this research, the focus is on the Chrome; therefore dangerous effects of chrome on health and different ways to eliminate it from cement are discussed. Chrome can have some unfavorable influences on concrete properties and when enters water pipelines have some toxic features for people when its concentration is high. Conventional solution could be the usage of ferrous sulfate and other similar materials. In this study zeolite is suggested to perform efficiently in concrete mixes to remove undesirable influences of Chrome in concrete. Additionally, appropriate dispose for refractory kiln bricks containing heavy metals and the sufficient control method for the cement kiln dust are proposed.

Keywords**—** Chromium, Cement, Cement Kiln Dust, Refractory Bricks, Zeolite.

I. INTRODUCTION

A heavy metal is a member of a loosely-defined subset of elements that exhibit metallic properties. It mainly includes the transition metals, some metalloids, lanthanides, and actinides. Many different definitions have been proposed—some based on density, some on atomic number or atomic weight, and some on chemical properties or toxicity. Some of them are dangerous to health or to the environment (e.g. mercury, cadmium, lead and chromium) some may cause corrosion (e.g. zinc and lead), some are harmful in other ways (e.g. arsenic may pollute catalysts). Within the European community the eleven elements of highest concern are arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, and thallium, the emissions of which are regulated in waste incinerators. Some of these elements are actually necessary for humans in minute amounts (cobalt, copper, chromium, manganese and nickel) while others are carcinogenic or toxic, affecting, among others, the central nervous system (manganese, mercury, lead and arsenic), the kidneys or liver (mercury, lead, cadmium and copper) or skin, bones, or teeth (nickel, cadmium, copper and chromium). It is notable that the focus of this study is on chrome.

According to the previous studies, the presence of heavy metals (especially chromium) in cement kiln is obvious [1], [2] and [17]. This results in some inappropriate properties of concrete and cement mixes containing chromium. Due to high temperature in cement kiln, refractory bricks are used to cover the walls. While low-chromium brick is currently more common in use today, refractory brick containing high levels of chrome have been used in cement kilns. Use of this refractory could contribute to a surge in chromium levels to the clinker during the first use of kiln after re-bricking [1]. Special procedures have to be done to dispose the hazardous bricks which contain heavy metals. In addition to increasing consumption of solid waste fuels, cement kiln operators have substantially increased the consumption of hazardous wastes as fuel, which has come to account for a significant portion of fuel consumption by cement kilns. Using these kinds of fuels can add more amounts of heavy metals to the existing resulted of raw materials in cement kiln dust. The objective of this paper is to review some practical methods of reducing harmful effects of chrome in concrete and also suggesting zeolite as a sufficient material which could trap chrome and neutralize undesirable performances of it. Furthermore, some propositions are presented to have a safe disposal of polluted refractory bricks and control methods of cement kiln dust.

II. CHROMIUM

Chromium is a steely-gray, lustrous, hard metal that takes a high polish and has a high melting point. It is also odorless, tasteless, and malleable. Chromium (Cr) is a metallic element that may occur in several valence states, including Cr^{-4} andCr^{-2} through Cr^{+6}. In nature chromium exists almost exclusively in the trivalent Cr (III) and hexavalent Cr (VI) oxidation states. Chromium was regarded with great interest because of its high corrosion resistance and hardness [3]. Trivalent chromium compounds (also Cr (III) or Cr^{3+}) are stable, and therefore the form found in quarried materials, and most prevalent in clinker and cement. Since these compounds are the most stable, having low solubility and low reactivity, their impact on the environment and living systems is low [1].

Siamak Bodaghpour, Assistant Professor, Civil Eng., Dept., Khaje Nasir Toosi University of Technology, Tehran, I.R.Iran (corresponding author to provide phone: +989124258802; e-mail: boudaghpour@yahoo.com).
Nader Biglari Joo, Research Assistant, Civil Eng., Dept., Khaje Nasir Toosi University of Technology, Tehran, I.R.Iran (phone: +989183174613; e-mail: nader.biglary@gmail.com).
Siavash Ahmadi, Research Assistant, Civil Eng., Dept., Khaje Nasir Toosi University of Technology, Tehran, I.R.Iran (phone: +989358352651; e-mail: siavashahmadi.66@gmail.com).

Hexavalent chromium (also Cr (IV) or Cr^{6+}) compounds are strong oxidizers and unstable. The form of particular interest is Cr (VI) due to its solubility in water. For example, when dissolved, Cr (VI) can penetrate unprotected skin and is transformed into Cr (III), which combines with epidermal proteins to form the allergen that causes sensitivity to certain people [1]. The natural or major sources of chromium in the earth's crust are in the trivalent state, but naturally occurring chromium compounds in the hexavalent state are rare and mostly man-made products [4]. The primary sources of chromium exposure are by breathing air, drinking water, eating food containing chromium or through skin contact with chromium or chromium compounds. For the general population, the most likely route of exposure to trivalent chromium is by eating foods that contain chromium, and trivalent chromium is identified as a natural essential nutrient for humans in many fresh vegetables, fruits, grain, meat and yeast. 50-200µg/d has been identified as an estimated safe and adequate daily dietary intake. However, hexavalent chromium is more easily absorbed by the body than trivalent chromium, but once inside the body system, hexavalent chromium is changed to trivalent chromium, that is essential for animals and humans, because it facilitates interaction of insulin with its receptor site, influencing metabolism of glucose, lipid and protein in its biologically active form. Chromium deficiency has been associated with atherosclerosis, cataract, growth failure, hyperglycemia, and neuropathy as well as with diabetes in human body due its vital role in metabolism of carbohydrates. Furthermore, effects such as acute tubular necrosis, kidney failure, and metabolic acidosis and in some cases death have been identified with accidental poisoning through hexavalent chromium compounds such as chromic acid and potassium tetra chromate [4]. Occupational exposure to chromium occurs mainly from chromate production, stainless steel production and welding, chrome plating, production of ferrochrome alloys, chrome pigment production and user industries, and from working in tanning industries. Sources in the air could be natural and anthropogenic. Natural sources may be continental dust flux, volcanic dust and gas flux. Anthropogenic are stationary point sources, including industrial, commercial, and residential fuel combustion, via the combustion of natural gas, oil, and coal, metal industries, such as chrome plating and steel production, cement-producing plants (cement contains chromium), the wearing down of asbestos brake linings that contain chromium, incineration of municipal refuse and sewage sludge, and emission from chromium-based automotive catalytic converters, cooling towers [5].

III. CEMENT PRODUCTION

Basically, cement is produced in two steps: in the first step cement clinker is produced from raw materials. In the second step cement is produced from the cement clinker. The first step can be dry, wet, semi-dry or semi-wet process, according to the state of the raw materials. The raw materials are crushed, and homogenized into a paste which is fed into the kiln. This is a kind of enormous rotating pipe, 60 to 90 m long and up to 6 m of diameter. This 'oven' is heated by a 200 °C flame to a temperature which can reach 1400-1600°C. The kiln is slightly inclined to allow materials to slowly reach the other end, where it is quickly cooled to 100-200°C. The final product of this phase is called 'clinker'. The second phase takes place in a cement grinding mill, which may be located in a different place from the clinker plant. Gypsum (calcium sulphates) and possibly additional raw materials are added to the clinker. All elements are ground (crushed) to lead to a fine and homogenous powder. The finished cement is then stored in silos before being delivered to users [6].

IV. CHROMIUM IN CEMENT AND HEALTH RISK

Chromium in the cement can originate from: 1) raw materials or fuel, 2) magnesia-chrome kiln refractory brick, if used, 3) wear metal from raw mill grinding process, if chromium alloys are used, and 4) additions such as gypsum, pozzolans, ground granulated blast furnace slag, mineral components, and cement kiln dust. The cement process, specifically kiln conditions, can influence how much Cr (VI) will form. The source of chromium input in the kiln feed is primarily as Cr (III). The conditions in the kiln include high amount of CaO, free lime, and alkalis due to the internal circulation of volatiles. Such conditions are favorable for oxidation of chromium to Cr (VI), the amount of which will depend on the oxygen pressure in the kiln atmosphere [1]. In the kiln, oxidizing atmosphere will play the largest role, with more oxygen in the burning zone leading to increased Cr (VI) formation. Alkali concentration is also of importance, since Cr (VI) in clinker is primarily in the form of chromates. In the finish mill, thermodynamically favorable conditions for oxidation to Cr (VI) exists, including high air sweep, moisture from gypsum dehydration, cooling water injection, and grinding aids, along with the high pH of the cement [1]. Portland cement contains Cr (VI), so operations that create concrete dust may lead to worker exposures. In one operation, the use of water to suppress dust during cleanup was observed to result in visibly lower dust concentrations. Dermal exposure to Cr (VI) through skin contact with Portland cement or other Cr (VI) containing products may lead to sensitization or allergic contact dermatitis. This condition, while not life-threatening, is debilitating and marked by significant discomfort and long-lasting adverse effects; it can have adverse occupational and social consequences and should be considered a material impairment to the health of affected workers. Occupational Safety and Health Administration (OSHA's) Advisory Committee for Construction Safety and Health (ACCSH) advised OSHA to include construction cement work under the proposed standard because of the known hazards associated with wet cement and the large number of workers exposed to wet cement in construction work settings. In particular ACCSH advised OSHA that only certain provisions might be necessary for workers exposed to wet cement (e.g., protective work clothing, hygiene areas and practices, medical surveillance for signs and symptoms of adverse health effects only, communication of hazards and recordkeeping for medical surveillance and training). Exposures can occur from working with a variety of construction materials that contain Portland cement. These include: concrete, mortar, stucco, and terrazzo. Examples of construction trades with potential exposure to wet cement include: bricklayers, cement masons, concrete finishers, construction craft laborers, plasterers, terrazzo workers, and tile setters. At a minimum, containers of water should be available to exposed workers so that they may wash skin that has come in contact with Portland cement (either dry or wet) [3].

V. UNDESIRABLE PERFORMANCES OF CHROME IN CEMENT MIXES

Concrete and cement mixes are a widely used material in the construction industry. However, heavy metals in cement can cause serious problems when exposed to human health matters. As an example, most of conveying pipe lines are made of concrete and cement materials. The cement-mortar lining is not considered a significant source of lead and chrome in drinking water. However, the recent practice of using Hazardous Waste Fuel (HWF) in cement kiln has raised the question of whether much more lead and chromium (and other metals) will leach out from the cement-mortar lining to drinking water. If the solubility of lead (at a pH equal to that of drinking water) in cement is larger than 70 ppb, the use of cement-mortar-lined pipes could cause the action level of lead in drinking water (15 ppb as established by the USEPA) to be exceeded. At the level of HWF burning in cement kilns prior to 1992, the action level for lead in drinking water is unlikely to be exceeded by using cement mortar- lined pipes. Also based on the modeled results, if the solubility of chromium (at a pH equal to that of drinking water) in cement is larger than 540 ppb, the use of cement-mortar-lined pipes could cause the Maximum Containment Level (MCL) of chromium in drinking water to be exceeded. At the level of HWF burning in cement kilns prior to 1992, the MCL of chromium (100 ppb as established by the USEPA) is likely to be exceeded by using cement-mortar-lined pipes if water is stagnant for two weeks and if no precipitation of chromium occurs. As a precaution at this time, cement with a Toxicity Characteristics Leaching Procedure (TCLP) concentration of lead larger than 70 ppb or an acid-soluble content of lead larger than 111 mg/kg is not recommended to be used for the lining of drinking water pipes; cement with a chromium TCLP concentration larger than 540 ppb or an acid-soluble content larger than 32 mg/kg is also not recommended. For one cement kiln studied, when HWF has the maximum allowable lead content, it is recommended that CKD not be fully recirculated. It is also recommended that the maximum allowable chromium content of HWF feed be lowered [7].

In addition to health problems, existing heavy metals such as chromium could cause some undesirable performances in concrete mixes. Results found by Barros and et al showed that the Cr_2O_3 additions to cement raw meal act as an inhibitor of C_2S formation and increase the amount of liquid phase. On the other hand, NiO has very little effect on the clinkering reactions, but NiO does cause a small increase in the temperature of C_2S formation and an opposite effect on the temperatures of liquid and the polymorphic transformation of C_2S. The production of Portland cement clinker in rotary cement kilns uses many sources of calcium, aluminum, silicon and iron oxides in the raw meal; although, not an essential element, chromium is always present in the charge. On average, 16 ppm of chromium are found in limestone and 100 ppm are found in clay. About 80 ppm of chromium is found in char and 50 ppm are found in oils, which are fuels used in rotary cement kilns. The use of bauxite as a source alumina may also increase the amount of chromium in the final product. The incorporated chromium is described as Cr_2O_3, and this compound reduces the viscosity of liquid during the process of clinker formation. Indeed, the most important effect of chromium additions on the Portland cement is the inhibition of the C_3S and C_2S formation. Chromium promotes distortions of the crystalline structure; also, Cr-O bonds are weaker than Ca-O bonds; thus, this explains the observed increase in the hydrating heat and cure time when chromium is present in the cement [2]. The presence of chromium slows down the hydration of limestone cement. This effect is a consequence of the interaction between chromium and Portland cement components, CrO_4^{2-} can substitute SO_4^{2-} forming a yellow chromium–ettringite: $Ca_6[Al(OH)_6]_2(CrO_4)_2.26H_2O$ since many ions of CrO_4^{2-} tend to assemble in the ettringite phase during ordinary Portland cement hydration. The addition of $CaCO_3$ modifies the vigorous initial reaction of C_3A with the water due the rapid formation of a barrier of hydrated calcium carboaluminate developed on the surface of C_3A grains. Consequently, the interaction between Cr and C_3A in the Cr–ettringite formation will be also modified in the limestone presence. The calcium monocarboaluminate formation is also influenced by the Cr (VI) presence. Its formation is slower and the formation of intermediate phases at early ages that possibly incorporate chromium was detected [8]. On the other hand, the presence of small quantities of Cr, during the clinkerization process increases the corrosion resistance and the durability of the Portland cement [9].

VI. ZEOLITE AND SUFFICIENT PERFORMANCES IN CONCRETE MIXES

Natural zeolite is a type of mineralogical material containing large quantities of reactive $SiO_2$and Al_2O_3. One important property of zeolite is the ability to exchange cations. This is the trading of one charged ion for another on the crystal. One measure of this property is the cation exchange capacity (CEC). Zeolites have high CEC's, arising during the formation of the zeolite from the substitution of an aluminum ion for a silicon ion in a portion of the silicate framework. During the 1970s, natural zeolite was shown to preferentially remove heavy metals such as Sr and Cs from wastewater, and this property made zeolite a preferred adsorbent for wastewater treatment systems. The selectivity of zeolite species, such as clinoptilolite and chabazite, for heavy metals based on the ionic radius and dissociation constant was in the order: $Pb^{2+} > Ni^{2} > Cu^{2+} > Cd^{2+} > Zn^{2+} > Cr^{3+} > Co^{2+}$. Maximum adsorption capacities of heavy metals for the zeolite was about two times greater than those of activated carbon irrespective of the kinds of metals [10].Clinoptilolite is a natural zeolite comprising a micro porous arrangement of silica and alumina tetrahedra. It forms as white to reddish tabular monoclinic tectosilicate crystals with a Mohs hardness of 3.5 to 4 and a specific gravity of 2.1 to 2.2. It commonly occurs as a devitrification product of volcanic glass shards in tuff and as vesicle fillings in basalts, andesites and rhyolites.

Zeolite is widely used in the cement industry in China as a cement blending material. Like other pozzolanic materials such as silica fume and fly ash, zeolite contributes to concrete strength mainly through the pozzolanic reaction with Ca (OH_2), thus the pozzolanic reactivity of this type of material in comparison with other pozzolans is of much interest. . Based on the experimental results (Poon and et al), it can be concluded that natural zeolite is a pozzolanic material, with reactivity between that of silica fume and fly ash. Generally, in blended cement pastes with lower water to cementitious materials ratio, the natural zeolite contributes more to the strength of the pastes. But in the pastes with higher water to cementitious ratio and a lower cement replacement level it undergoes a higher degree of reaction. Partial replacement of cement by zeolite can improve the properties of concrete by increasing concrete strength and preventing undesirable expansion due to alkali-aggregate reactions. Also, it has been reported that zeolite reduced the porosity of the blended cement pastes and improved the interfacial microstructure properties between the blended cement paste and the aggregate in the produced concrete [11]. In addition, Sammy and et al showed that zeolite decreased bleeding and increased marginally the viscosity of concrete without significantly compromising the slump. And at 15% replacement level, it resulted in 14% increase in concrete strength at 28-day compared with the control concrete. The test results also showed that there existed an optimum replacement level for zeolite to affect a decrease in initial surface absorption and in chloride diffusion of concrete. The micro-structural study on concrete with zeolite revealed that the soluble SiO_2 and Al_2O_3 could react with Ca $(OH)_2$ to produce CSH which densified the concrete matrix. Pozzolanic effect of zeolite improved the microstructure of hardened cement paste and reduced the content of the harmful large pores, hence made concrete more impervious. Zeolite was capable of controlling slump loss of high strength concrete when it was used as a carrier for super plasticizer and plasticizer [12].

VII. WAYS TO DECREASE HARMFUL EFFECTS OF CHROME IN CONCRETE

Several materials have been used to reduce the level of soluble Cr (VI) formation. The most widely used material is ferrous sulfate; other materials include stannous sulfate, manganese sulfate, and stannous chloride [1]. Some of these materials have limitations such as limited stability, limited supply, and possible influence on cement performance. In all cases, some form of dosing and mixing equipment is required. This study suggests the usage of zeolite as a pozzolanic material when the quantity of chrome seems to be high. With this replacement, some negative effects of Cr such as mechanical properties could be treated due to efficient performance of zeolite. Also the chance of trapping heavy metals such as chromium is considerable. Also further researches are needed to find an absolute conclusion.

VIII. DISPOSING REFRACTORY BRICKS COMMENTARY AND CEMENT KILN DUST

Under the RCRA of 1976, the term hazardous waste means a solid waste, or combination of solid wastes, that, because of its quantity, concentration, physical, chemical, or infectious characteristics, may cause or significantly contribute to an increase in mortality or an increase in serious irreversible or incapacitating reversible illness or pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of or otherwise managed [13]. Chromite-containing refractory is used to line furnaces and kilns for production of copper, nickel, cement and glass. Refractory in cement kiln (including free chromium or other types) can adsorb quantities of heavy metals (chromium) exist in the kiln. These refractory bricks can satisfy the definition of hazardous wastes and specials considerations should be applied. Metals are considering among the most dangerous environmental pollutants, because they do not disintegrate with physical processes and therefore remain for longtime period. They affect biogeochemical cycles and accumulate within living organisms, eventually making their way to humans through the food chain, where they can cause perturbation to biological reactions, long lasting harm to vital organs or even death [14]. It is estimated that about 400 tons of mercury, 3000 tons of cadmium, 14,000 tons of nickel, 20,000 tons of copper, and nearly 100,000 tons each of chromium, lead, and zinc are disposed in landfills each year in the U.S. [15]. To dispose these contaminated refractory bricks, landfills must include an impermeable layer (a liner) that separates the landfill and its contents from the soils and bedrock below, and a system to collect and treat any liquids that seep from the landfill (a leachate collection and removal system). Modern landfills typically treat their leachate to remove metals, bacteria, biological oxygen demand (BOD), and chemical oxygen demand (COD) before discharging to surface water, or they send the leachate to a publicly-owned treatment works (POTW). When landfills have reached their capacity limits, they are “closed.” Closure typically includes installation of a relatively impervious cover, grading of the surface to facilitate water movement away from its surface, and monitoring of groundwater for 30 years. In many cases, landfills also have a gas collection and venting system, which may include combustion of the landfill gas or pumping of the gas offsite to be used as fuel [15].

The data show that landfill leachate generally contains higher levels of heavy metals than allowed by drinking water standards and groundwater maximum contaminant levels. If a landfill’s containment system fails, it could threaten ground waters or surface waters. Landfills located above fractured rock or cavernous limestone aquifer systems could be especially problematic [15]. Monitoring of the air, surface water, and groundwater for as long as the waste remains a threat to the public health and the environment is an essential component of any site.

It is remarkable that hazardous waste landfills should be located well above historically high groundwater tables. Care should be taken to ensure that a location has no surface or subsurface connection, such as a crack in confining strata, between the site and a water course. Hydrologic considerations limit direct discharge of wastes into groundwater or surface water supplies [16].

Cement Kilns are horizontal rotary kiln, inclined rotating cylinders that are refractory lined, internally fired, and designed to produce clinker through the intense heating of raw materials. Raw materials are fed into the upper, cool end while fuels are normally fed into the lower, hot end. All the gases and dusts produced in the cement kiln, exit the kiln under the influence of induced draft fans. The components of these gases are derived from the combustion of fuels, contaminants (organic and inorganic) in the kiln solids, small particles of feed and clinker material.

Cement Kiln Dust (CKD) is comprised of thermally unchanged raw materials, dehydrated clay, decarbonated (calcined) limestone, ash from fuel, and newly formed minerals, with diameters ranging from near zero to greater than 50µm. Some of these elements and compounds like heavy metals are toxic and harmful even at low concentrations. Furthermore, the use of hazardous waste and other wastes and raw materials as fuel and raw material inputs in cement kilns has raised concerns regarding the concentrations of certain heavy metals in CKD generated. Part of this CKD recycle back to the kiln system (Recycle CKD) and most of it disposed in an on-site waste management unit, or sold or given away for beneficial use (Net CKD).

Using hazardous waste has different effect on CKD generation, according to the cement kiln type. Wet kilns that burn hazardous waste fuels generate about 22 percent more CKD per ton of product than those that do not burn hazardous wastes. In the case of dry kilns, the data suggest the opposite. Dry kilns that burn hazardous waste generate about 7 percent less gross CKD per ton of product. On the other hand, using hazardous waste fuel generates almost twice Net CKD per ton of product.

According to EPA survey, the chromium was consistently present (although at variable concentrations) in all CKD samples collected from different kilns. Chromium is found at mean concentration in as generated CKD that is 2.4 time higher in dust from facilities burning hazardous wastes than in CKD from facilities not burning hazardous waste fuels.

According to EPA data, the maximum concentration of chromium in 277 CKD sample was 1.29 ppm that is well below its corresponding regulatory standard (5 ppm).

Air pollution control devices (APCD) are used to limit dust emissions from the kiln system to the atmosphere. Among all APCD that EPA suggested, electrostatic precipitators and fabric filters seems to be more efficient. Preceding these two APCD by one or more cyclones could have better result.

APCD	Description
Electrostatic Precipitators	One or more high intensity electrical fields are generated and cause particles to acquire an electrical charge. These charged particles migrate to a collecting surface that has the opposite electrical charge. The collecting surface may be wet or dry. Facility operators then retrieve the captured CKD. One advantage of this technology is that flow is not restricted during collection. Collection efficiencies can be as high as 99.75 percent.
Fabric Filters	Filters remove particulate matter from gas streams by retaining the particles in a porous structure, and are typically used in series to form a bag house. The porous structure is generally a woven or felt fabric with a retention efficiency that improves as the interstices fill with captured dust, but with the negative effect of increased flow resistance. Thus, regular filter cleaning is required to maintain efficiency. Bag house filters can also be constructed of siliconized glass fibers (i.e., fiberglass). Fabric filters can remove submicron-sized particles at collection efficiencies as high as 99.95 percent.
Cyclones	A vortex within a collector propels particles to deposition areas for removal. Cyclones may be operated either wet or dry. They deposit the collected particulate matter into a hopper for eventual collection. Cyclones have collection efficiencies that range from 58 to 97 percent. Multiple cyclones used as part of one unit are referred to as multiclones. Multiclones have collection efficiencies that range from 85 to 94 percent for dust particles with diameters of 15 to 20 microns.

IX. SUMMARY

Heavy metals are among carcinogenic or toxic elements in the world. Existence of heavy metals (especially chrome) in cement kiln is unavoidable. Using cement containing high amounts of Cr can cause unpleasant mechanical or durability performances of cement or concrete mixes. In addition, when solubility of Cr in cement-mortar-lined pipes is larger than 540 ppb could cause MCL to be exceeded. On the other hand, zeolite as an adsorptive of heavy metals can be used in cement to trap heavy metals and also modify their undesirable properties. One of the big problems related to existence of heavy metals in kiln, is the disposing the refractory bricks used in kiln, which should include an impermeable layer that separates the landfill and its content from soil and bedrock below, and a system to collect treat any liquid that seep from the landfill. Furthermore, controlling the dust emitting from cement kiln is necessary. Among all APCD that EPA suggested, electrostatic precipitators and fabric filters seems to be more efficient. Preceding these two APCD by one or more cyclones could have better result. .

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