Challenge the very concept of a development strategy which places the search for dollar over issues of justice and equity for humans... or survival of tigers.

— Medha Patkar

CHAPTER 5

TOXIC METALS DEPOSITION ON SURFACE SOILS IN THE VICINITY OF A SLAG BASED CEMENT PLANT

: ENVIRONMENTAL IMPACTS OF CEMENT PLANTS

: SOLUBILISATION OF METAL OXIDES BY HUMATES OF SOILS
5.1 INTRODUCTION

From the point of view of air pollution, the cement industry, all over the world, is placed in a somewhat unique situation. By its very nature of location, which is always as near the quarry as possible, a cement plant is always away from the urban areas. But again, because of its very nature of activities i.e., crushing, grinding, handling, conveying, drying, calcining etc., the generation of pollutants in the form of particulates is not only unavoidable but also profuse in nature.

It has been ascertained from various statistics that the total dust losses in a cement plant can be quite substantial. In a wet process plant with a production capacity of 1600 TPD, the dust loss may be as high as 100 TPY from the kiln alone. For a dry process plant of 1000 TPD capacity, the same can be of the order of 200-250 tonnes per year. All these are after making the use of sophisticated dust collection equipments, like electrostatic precipitators. In the raw mill drying and grinding section, the loss can be as high as 2000 TPY, for a plant of about 150 TPH capacity. For clinker grinding, it can go to the extent of about 20 TPY with a production capacity around 50 TPH. Again all these figures are applicable after the use of dust collectors. Although the cement production in India has grown at a steady rate since independence, its per capita consumption is yet around 23 kg compared to about 500 kg in many of the advanced countries (1). The cement production in the country in year 94-95 was 62.9 MT(2), and the same is likely to touch 100 MT per annum by 2000 AD. The studies described here are related to a slag based cement plant located at Jamul (Distt. Durg, M P). The process details and the emission sources of the plant have been shown in Fig 5-1. The fallout of the settleable dusts related to this plant was studied by an
earlier worker who reported the dust fallout rates, in an area 8 km x 8 km, in the range of 464.00 - 964.24 metric tonnes/km²/month at a distance of 1 km around the plant. Those at distances of about 2 - 2.5 km ranged between 178.81 - 978.30, and those at distances of 4 km ranged between 34.16 - 572.10 metric tonnes/km²/month. The data were based on measurements at 20 sampling sites during the post-rainy period (October-March) (3). The collected samples were also chemically analysed and the toxic metals concentrations in them were found as follows: (in ppm) Hg - 0.05 (1), Bi - 18.50, Cd - 3.80, Co - 70.00, Cu - 70.75, Ni - 250.70, Pb - 61.50, Sb - 36.50, Zn - 111.30, Mn - 2122.50 (4). The settleable dust was also reported to contain other elements such as Al, Cr, Fe, Mo, V and alkali and alkaline earth metals (1). The toxic metals which were reported to be present in the settleable dusts of a cement plant have also been reported to be present in the suspended particulate matter in the vicinity of a cement plant (5). Sengar and co-workers have reported the daily mercury emission from the kilns of a cement factory at the rate of 343 g/day mostly originating from coal and limestone (6).

5.2 CEMENT PLANTS: THEIR IMPACTS ON ENVIRONMENT

Cement kiln dusts have been frequently reported as adversely affecting the plants when deposited on a moist leaf surface. Observations of injury on sensitive plant species have provided a means of monitoring pollutant emissions from a source, and observations on plant injury have also been a valuable tool for determining the geographical distribution of a pollutant over a large area (7). Besides polluting the soils, the cement dust pollution has been reported to affect the yield of cotton (8), and also reduced the chlorophyll content in a number of
Fig. 5-1 FLOW CHART OF A PORTLAND SLAG CEMENT PLANT SHOWING EMISSION POINTS
Mishra and co-workers have reported the impact of cement dusts on soil characteristics, and the chlorophyll (10). Prasad and co-workers have reported the adverse effect of cement kiln dust on the crop of black gram (*Vigna mungo*) (12). Tandon and co-workers have reported the presence of heavy metal, (Mn, Cr, Pb) even in urinary excretions of cement workers (13). Agrawal and co-workers have reported injury symptoms on certain plants, growing within a radius of 2 km from the source (14). Reduction in chlorophyll content in maize leaf polluted by cement kiln dust has been reported by Pandey and co-worker (15). Banerjee and co-worker have reported the calcification of surface soils in the vicinity of a cement plant (16). Gunamani and co-workers have reported the adverse effects of deposited cement dusts on the morphology and anatomy of plants (17, 18).

It is in the context of the above-stated observations that a plan to study the levels of occurrence of selected toxic metals (Hg, Pb, Cu, Co, Ni, Mn and Cr) in the surface soils in the vicinity of a cement plant was taken in hand. The slag based cement plant selected here for the studies is located at Jamul (Distt Durg, M.P.). The plant has a production capacity of 1.78 MT per annum. The plant was established in 1965. The cement plant kilns use both semi-dry and dry techniques of cement manufacture. The raw materials consumption in the plant is as follows: Lime stone 0.79 MT, Steel slag 0.62 MT, Coal 0.16 MT, and Gypsum 0.07 MT.
5.3 CEMENT PLANT DUST FALL OUT: STUDIES OF TOXIC METALS DEPOSITION AND MINERALOGIC COMPOSITION OF SURFACE SOILS IN ADJOINING AREAS

INTRODUCTION

In the work being reported here, samples of the settleable dusts emitted by the cement plant and those of surface soils were collected at distances up to 10 km from the cement plant, and the concentrations of some key elements were determined in them to arrive at a conclusion with regard to the gradual changes in the mineralogic compositions in the surface soils around the cement plant as a result of the particulate emissions arising from the cement plant.

MATERIALS AND METHODS

Collection of Settleable Dusts: Four sampling sites within a distance of 1 km from the cement plant were selected in each direction with respect to the cement plant. Four dust jars of polythene, cylindrical in shape having 17 cm diameter and 20 cm height were used for the dust collection (19). 1 ml of 1% CuSO₄ solution was added to each of the jars as fungicide and algacide (20). Distilled water was placed in each of the collectors to cover evaporation losses during the period of collection. The collectors were then placed in position 5-10 m above the ground (21). After a duration of 30 days, the jars were brought to the laboratory and the collected dust used for analysis.

Collection of Soil Samples: Soil samples were collected from ten sampling sites by digging up to 30 cm depth at each site. A soil sample of the same geochemical
composition was collected from an apparently uncontaminated area. The locations of the sampling sites and their distances from the cement plant have been shown in Fig. 5-2 and Table 5-1.

**Analysis of the Dust and Soil Samples**: Selected major elements (Fe, Ca, Mg, Na, Mn and Cr) and minor elements (Hg, Pb, Cu, Ni and Co) were determined in each sample. Fe was determined titrimetrically using KMnO₄, and Ca and Mg were also determined titrimetrically using EDTA (disodium salt) solution as described earlier (Section 4.3). Mn, Cr, Pb, Hg, Cu, Ni and Co were determined spectrophotometrically using standard procedures (22,23), as described earlier (Section 3.3). Sodium was determined flame photometrically (22) as described earlier (Section 4.3).

The chemical reagents used were Analysis Grade (BDH AnalR). The water used was deionised and distilled. The glasswares used were superior quality borosilicate.

The results obtained have been shown in Table 5-1.

The meteorological data of the area of study were as follows: highest temperature - 43.8°C, lowest temperature - 10.6°C, rain fall - 1309.8 mm, maximum wind velocity - 8.60 km/h, minimum wind velocity - 2.87 km/h, wind direction - irregular before monsoon, northerly and north westerly in midwinter, and south westerly during rest of the year.
Fig. 5-2: Site Location Plan of Jamul Cement Works
TABLE 5-1 CONCENTRATIONS OF SELECTED ELEMENTS IN CEMENT PLANT DUSTS AND SURFACE SOILS

<table>
<thead>
<tr>
<th>Elements analysed</th>
<th>Cement plant dust sample*</th>
<th>Surface Soil Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td>0.5 km</td>
<td>0.75 km</td>
</tr>
<tr>
<td>Major Components (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>2.32</td>
<td>3.88</td>
</tr>
<tr>
<td>Ca</td>
<td>9.70</td>
<td>4.80</td>
</tr>
<tr>
<td>Mg</td>
<td>5.80</td>
<td>3.18</td>
</tr>
<tr>
<td>Na</td>
<td>0.22</td>
<td>0.40</td>
</tr>
<tr>
<td>Mn</td>
<td>0.21</td>
<td>0.18</td>
</tr>
<tr>
<td>Cr</td>
<td>0.22</td>
<td>0.04</td>
</tr>
<tr>
<td>Minor Components (mg/kg)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.1</td>
<td>7.2</td>
</tr>
<tr>
<td>Pb</td>
<td>60.0</td>
<td>110.0</td>
</tr>
<tr>
<td>Cu</td>
<td>71.0</td>
<td>118.0</td>
</tr>
<tr>
<td>Ni</td>
<td>251.0</td>
<td>86.0</td>
</tr>
<tr>
<td>Co</td>
<td>70.0</td>
<td>38.0</td>
</tr>
</tbody>
</table>

*Average Values  **Nil Denotes Undetectable
RESULTS AND DISCUSSION

The wind direction in the area of study was found to be irregular before monsoon, northerly and north-westerly in mid-winter and south-westerly during rest of the year. Accordingly, the sampling site nos. 2, 3, 4, 5, 7 and 8 were found to be more susceptible to receive a higher fallout of the dust compared to sampling site nos. 6 and 9 situated in the east direction with respect to the cement plant (Fig. 5-2). Further, site nos. 1, 2, 3, 4 and 5, situated up to a distance of 1 km had a higher susceptibility of receiving the fallout matter compared to site nos. 6, 7, 8, 9 and 10 situated at longer distances (Fig. 5-2). These inferences have been confirmed by the soil analysis data of the area of the study. Fe, Ca, Mg, Na, Mn and Cr were found to be the major components of the settleable dust emitted by the cement plant. The occurrences of these elements in the dusts is in conformity with the nature of the raw materials, namely steel plant slag and limestone, which were being used in the plant. The coal fly ash, on account of its consumption in this plant, also joins the emitting particulates. When the occurrences of these elements in the surface soils were observed, a progressive decrease in the concentrations of these elements in the surface soils with increasing distance from the cement plant was found. A similar observation has also been found in the cases of selected minor elements (Hg, Pb, Cu, Ni, Co) which were found to be present in the settleable dust and also in the surface soils. An appraisal of the data suggests that the surface soil up to a distance of 4.5 km have received profuse depositions of the cement plant dust, which resulted in a significant change in the mineralogic composition of the surface soils. The percent increase in the concentrations of the major components and minor components in the surface soils at a distance of 1 km from the cement plant, compared to the concentrations of these components in the soils from apparently uncontaminated
areas (situated 20 km away) was found as follows: Fe - 28.50%, Ca - 81.60%, Mg - 85.10%, Na - 75.00%, Mn - 28.50%, Cr - 66.67%, Pb - 45.45%, Cu - 42.50%, Ni - 37.17%, Co - 38.46% Mercury, which was at undetectable level in the uncontaminated soil was found to have appeared at a level of 4.2 ppm in the contaminated soil at this distance. The alterations in the mineralogic composition, in diminishing magnitudes have been found up to a distance of 9.5 km from the cement plant. The entry of the extraneous elements of toxic nature (Hg, Pb, Cu, Ni and Co) into the surface soil was found to add an additional concern in view of the probable uptake of these toxic elements by the crops and vegetation grown in these areas.

5.4 HUMATES OF PADDY SOIL: STUDY OF THEIR SOLUBILISING EFFECT ON SOME METALLIC OXIDES OF MINERALOGIC ORIGIN

INTRODUCTION

The total paddy-cultivated area in Raipur, Raigarh, Durg, Bilaspur and Sarguja districts of the Chhattisgarh region is more than 38 lakh hectares (24). The soils of the region have been divided in four categories locally called as Bhata, Matasi, Dorsa and Kanhar. On the basis of micronutrients and other soil parameters, the Kanhar variety of the soil is known to be most suited for the paddy crops. It is widely recognised that humic substances present in soils form linkages of various kinds with metals through ion-exchange, adsorption on surfaces and formation of chelates (25) Metal oxides of mineralogic origin present in soils have their specific roles in the plant growth (26) When these oxides start

getting deposited extraneously over surface soils through industrial operations, a progressive enrichment of the surface soils in respect of the incoming metal oxides is an unavoidable consequence. A field study carried out in the vicinity of a steel plant showed iron in the range of 15000-65000 mg/kg in the soils compared to 11300-12800 mg/kg in the uncontaminated area having soils of the same geochemical composition. The enrichment of other metals in the same area was found as follows: Ni, Hg and Cu -more than 2-fold; and Mn and Co -more than 3-fold; Cd -4-fold; Pb -more than 7-fold and Cr -more than 8-fold. There have also been reports of several toxic metals being found present in the dust fallout arising from mineral based industries such as phosphatic fertilizer plant (27-29), steel plant (30-32), cement plant (33,34) and thermal power plant (35, 36). It needs to be investigated as to how extraneous metallic oxide particles interact with the humic components of the soils in their natural physico-chemical states.

In the work reported here, the relative reactivity of the humates isolated from paddy soil towards selected metallic oxides in their natural mineralogic states, has been investigated.

**MATERIALS AND METHODS**

**Sample Collection**: Three farm fields situated in the area of Kanhar variety of paddy soils were identified in a village in the Raipur Tehsil. Samples from the fields were collected by the prescribed procedures, and then composited (37) Analyzed samples of iron-ore (Fe 69.1%), pyrolusite ore (Mn 51.2%), chromite ore (Cr 29.5%) and copper oxide ore concentrate (Cu 28.6%), supplied by Bureau of Analyzed Samples Limited, Yorks, (U K.) were used.
Humic Acid Extraction from Soil: A weighed quantity (600 g) of the soil was mixed with 3 litres of sodium pyrophosphate solution (0.1M) in 0.1M NaOH medium (pH 13.0). The supernatant was acidified with H$_2$SO$_4$ to a pH of 1.5 which yielded precipitated humic acid. The product was purified by repeated flocculation and peptisation using dilute H$_2$SO$_4$ and NaOH till free from metal and sulphate ions. The product was further purified in a batch of flasks containing Dowex-15 cation exchange resin until no further decrease in its pH was noticed. The ash content in a small portion of the purified humic acid was determined by the usual procedure (38, 39).

Humate - Metal Oxide Interaction Studies: Weighed quantities (100 mg each) of the purified humic acid were taken separately in 250 ml stoppered bottles and treated with dilute NaOH solution with magnetic stirring to obtain the humates in the soluble form, and volume of the solutions adjusted to 100 ml. Weighed quantities of the analysed samples of oxide ores each containing 10 millimoles of the principal metallic element (iron ore - 0.8110 g; pyrolusite ore - 1.0720 g; chromite ore - 1.7590 g; copper ore - concentrate - 2.5410 g) were added separately to the bottles, and the pH adjusted to 7.0. The reaction mixtures were placed at room temperature (28 ± 2°C). Aliquots (1 ml each) were withdrawn from each mixture at intervals of 1 day, and the principal metal ions (Fe, Mn, Cr and Cu) were determined spectrophotometrically. The reagents used were: Sodium diethyldithiocarbamate (0.2% solution in water) for Cu, potassium thiocyanate (20% solution in water) for Fe, potassium periodate (powder form) for Mn, and diphenylcarbazide (0.25% solution in 50% acetone) for Cr (22, 23). The measurements were continued for nineteen days when almost static values of the metal concentrations were obtained. The results obtained have
been shown in Table 5-2. The relationship between the period of interaction and the concentration of the respective metal ions have been shown in Fig. 5-3.

**CEC Determination of Soil**: A weighed quantity (5 g) of the soil was mixed with 50 ml sodium acetate solution (1 N) at pH 5.0 in a centrifuge tube, and the suspension was digested in water bath for 30 minutes. The salts were removed by centrifugation. Two additional washings using the same solution were also done. The sample was then given 5 washings using CaCl₂ (1 N) solution. The excess salt was removed by washing with acetone solution (80%) till free from chloride. Finally the calcium ions were replaced by giving 5 washings with a neutral solution of ammonium acetate (1 N). The calcium was then determined in solution using flame photometer (Systronics Model 305) (37). The value obtained has been described under Results and Discussion below:

**RESULTS AND DISCUSSION**

The results showed that the paddy soil used here contained humic acid to an extent of 0.85%, and the ash content of the isolated product was found to be 0.22%. The CEC of the soil was found to be 38.30 meq/100g. The following informations have been obtained from the experimental data shown in Fig 5-3.

(i) The oxide ores containing Fe, Mn, Cr and Cu as the principal metallic elements are not inert, and have finite capacity of reacting in their solid states with the humates of the paddy soil in its natural pH conditions. There are reports that the humates of the soils remove the metal ions through the process of ion exchange and complexation. The complexation is promoted by
### TABLE 5-2 SOLUBILIZATION OF METALLIC OXIDES BY HUMATES OF PADDY SOIL

<table>
<thead>
<tr>
<th>S. no.</th>
<th>Metal-ions used</th>
<th>Concentrations (m moles)* found in duration of</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 day</td>
</tr>
<tr>
<td>1.</td>
<td>Fe (III)</td>
<td>0.0045</td>
</tr>
<tr>
<td>2.</td>
<td>Cu (II)</td>
<td>0.0094</td>
</tr>
<tr>
<td>3.</td>
<td>Cr (III)</td>
<td>0.0048</td>
</tr>
<tr>
<td>4.</td>
<td>Mn (IV)</td>
<td>0.0137</td>
</tr>
</tbody>
</table>

* Room temperature 28±2°C

** Measurements were omitted on account of very slow rate of reaction
Fig. 5.3 Solubilization of metallic oxides on interaction with humates of soil
The groups such as hydroxy, carboxylic, amide, thio-amide which have been found to be present in the humic acid isolated from the paddy soil of the variety used in the studies here (40). The process of complexation can thus be attributed to the solubilisation of the ores used here.

(ii) The highest reactivity (on mole basis) has been observed in the case of cupric oxide. The relative reactivities under identical reaction conditions have been found in the following order: Cu > Fe > Cr > Mn.

(iii) The reaction products have been found to be of soluble nature in each case of the oxides used here. The interaction studies do not, however, preclude the probability of the formation of the products of insoluble nature under the experimental conditions used here. The soluble nature of the products suggests that the metallic elements of the oxide ores are rendered mobile on interaction with the humates of the soil.

(iv) The experimental conditions are suggestive of the chelation process between the donor atoms of the humates and the respective metal atoms.

(v) The progressive deposition of the extraneous metallic oxides on paddy soils should thus suggest that substantial functional capacities of the normal humates of the surface soil are engaged by the incoming metallic oxides emitted by mineral based industries such as steels, cements, thermal power, fertilizers and ore smelters. In conclusion, the factor of the deposition of the particulate matter of mineralogic origin on paddy soils requires to be viewed during the soil conservation and its management.
SUMMARY

This chapter was devoted to the study of the enrichment of toxic metals in surface soils arising through the deposition of settleable dusts emitted by a cement plant. The studies began with a survey of dust emission capacities of cement plants. An appraisal of the fallout of settleable dusts, and the toxic metal contents of the dusts of the cement plant under study was made through a survey of literature. A further appraisal of the adverse effects of the cement plant fly ash on soils, crops and vegetations was made through the literature survey.

Samples of settleable dusts at four sites, each 1 km away from the emission sources were collected by the prescribed procedure. Ten samples of surface soils upto a distance of 9.5 km from the cement plant were also collected. One soil sample from an apparently contamination-free site, situated 20 km away, was also collected. The concentrations of major components (Fe, Ca, Mg, Na, Mn, Cr) and minor components (Hg, Pb, Cu, Ni, Co) were determined in each sample by standard procedures. The meteorological data of the area of study were also recorded. The data obtained showed that the levels of occurrences of the major and minor components in the surface soil samples upto a distance of 9.5 km were significantly enhanced in comparison to those in the uncontaminated soil. The occurrences of these components were found to decrease with increasing distance from the emission sources. The probability of the uptake of the toxic metals by the crops and vegetations grown in the contaminated areas was discussed.

As a logical follow up, the interaction of selected metallic oxides of mineralogic origin e.g. oxides ores of Fe, Cu, Cr and Mn with the humic acid
isolated from a sample of paddy soil was studied in detail. For this purpose, the 
humic acid contents of paddy soils (Kanhar variety) were extracted, and purified 
using the prescribed procedures. Known quantities of the humic acid were made 
to interact with calculated amounts of analysed samples of iron ore, pyrolusite 
ore, chromite ore and copper ore-concentrate, each containing 10 millimoles of 
the principal metallic element. The interaction was carried out in aqueous medium 
at pH 7.0. The concentrations of the metals (Fe, Mn, Cr and Cu) in the 
supernatant were determined spectrophotometrically. It was found that the 
humates of the paddy soil had a leaching effect on each of the oxide ores. The 
relative solubilisation of the oxide ores with the humate was found in the 
following order: CuO > Fe₂O₃ > Cr₂O₃ > MnO₂. The studies suggested that the 
incoming metallic oxides had finite capacities to interact with the humic acid of 
the soils resulting in the formation of water soluble products. The metallic 
elements present in the insoluble solid phase are thus rendered mobile as a result 
of such interaction.
REFERENCES


