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# Chemical, Physical, Mineralogical, Morphology and Leaching Characteristics of a Thermal Power Plant Air Heater Washing Waste

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**ABSTRACT:** Most of electricity is generated by thermal power plants in Iran. Shahid Rajaee thermal power plant consists of four 250MW natural gas and fuel oil burning units that is located at 100 km west off Tehran. As a result of fuel oil burning in winter time, boilers air heaters are washed and cleaned frequently. The wastewater originating from air heater washing contains suspended solids and different dissolved heavy metals particularly V, Ni, Zn, Cr, Pb. Wastewater is then treated in effluent treatment plant by chemical precipitation followed by centrifugal dewatering of sludge. Waste from this process contains significant amounts of heavy metals and is considered as specific industrial wastes that should be more characterized under specific wastes act of Iran. For the first time in Iran, in the present investigation seven composite samples from air heater washing wastewater treatment dewatered sludge were subjected to chemical composition, mineralogy and leaching characteristics studies to better understand the physical and chemical characteristics of this kind of wastes. Regarding fuel oil constituents and environmental impacts of metals the most likely pollutants which would be of concern in this study were heavy metals (Cd, Co, Cr, Mn, Ni, Pb, Zn and V). Results revealed that mean pH, wet and dry density and moisture content of the waste are 6.31, 1532 kg/m$^3$, 1879 kg/m$^3$ and 15.35 % respectively. Magnetite, $SiO_2$, $P_2O_5$, CaO, $Al_2O_3$ and MgO were the main constituents of the waste with the weigh percent order of 68.88, 5.91, 3.39, 2.64, 2.59 and 1.76% respectively. Toxicity Characteristic Leaching Procedure (TCLP) test results for some heavy metals showed that mean elemental concentrations of Cd, Co, Cr, Mn, Ni, Pb, V and Zn in leachate were 0.06, 1.55, 5.49, 36.32, 209.10, 0.58, 314.06 and 24.84 mg/lit respectively. According to specific wastes act of Iran this waste can be classified as hazardous due to presence of heavy metals and leaching characteristics and should be disposed regarding hazardous waste disposal considerations.

**Key words:** Power plant, Waste, Heavy metals, Leaching test, Characterization

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## INTRODUCTION

Most of electricity is generated by thermalpower plants in Iran. In most of those thermal power plants usually natural gas is burnt from spring to late falls. As a result of increased municipal consumption of natural gas and consequently its pressure loss during late fall and winter time in Iran, fuel oil is burnt to generate electricity in thermal power plants of Iran during this time of the year (Iran MOE, 2005). In thermal power plants, combustion air flow is preheated via heat transfer from exhausting flue gas before flowing into the furnace. The air heaters in thermal power plants are indirect heat transfer devices that transfer energy from flue gas to entering fresh air in order to increase energy generation efficiency (El-Wakil, 1985). Due to existence of particulate matters in flue gas and scaling of heat transfer surface, air heaters should be washed and cleaned frequently. The wastewater originating from air heater washing contains suspended solids and different dissolved heavy metals particularly V, Ni, Zn, Cr, Pb and other constituents of fuel oil and heat transfer surface alloy (Elliott, 1989). This wastewater is then treated in effluent treatment plants by precipitation with soda or lime technology in Iranian thermal power plants. Sludge from this process that is then dewatered by centrifugal, pressure or vacuum filtration contains significant amounts of heavy metals and is classified as specific industrial wastes and should be more characterized (i.e. toxicity leaching characteristics) under specific wastes act of Iran (Iran DOE, 2005). Release of heavy metals from this waste into the environment will have potentially negative impacts on soil, groundwater and surface water quality as well as human health. Regarding Iranian regulations if the waste categorized as hazardous, facility owners are not allowed to dispose or landfill them in municipal solid waste landfills unless they are stabilized. For development of a more efficient stabilization method, waste characterization studies should be conducted first. Characteristics of different stabilized and unstabilized wastes have been studied by many researchers from chemical/ physical/ leaching and mineralogical points of view (Coz, 2004; Magalhaes *et al.*, 2005; Li, 2004; Saikia, 2005; Cohen and Petrie, 2005; Asokan, *et al.*, 2005). Although heavy metals containing wastes as well as combustion residues chemical composition and leaching characteristics have been studied before (Eighmy, 1995; Lopes *et al.*, 2001; Kirby and Rimstidt, 1994; Wiles, 1996; Forestier and Libourel, 1998; Li, *et al,*. 2004; Saikia, *et al.*, 2005; Sophia and Swaminathan, 2005; Park, 2000; Bagnoli, *et al.*, 2005), most of thermal power plant wastes that have been characterized were combustion residues or those originating from coal fired power plants (Asokan, *et al.*, 2005) and no research results on this specific type of waste has been found in literature. Shahid Rajaee thermal power plant consists of four 250MW natural gas and fuel oil burning units that is located at 100 km west off Tehran. Air heater washing wastewater in Shahid Rajaee thermal power plant is treated by coagulation/precipitation by alum and lime. For the first time in Iran in the present investigation seven composite samples from air heater washing wastewater treatment dewatered sludge were subjected to chemical composition, mineralogy, electron microscopy and leaching characteristics studies. Regarding fuel oil heavy elemental constituents and environmental considerations the most likely pollutants which would be of concern in this study were heavy metals (Cd, Co, Cr, Mn, Ni, Pb, V and Zn).

## MATERIALS & METHODS

SamplesThirty five waste samples were taken from dewatered sludge originated from air heater washing wastewater precipitation in Shahid Rajaee thermal power plant in January 2005. It should be pointed out that this particular kind of wastes is generated in batch types and occasionally during a year usually when air heaters are washed in wintertime. Collected samples were stored cool in the sealed bags for analysis. Seven composite samples were prepared by homogenizing and combining every five samples.

## PHYSICAL AND CHEMICAL PROPERTIES

Samples were air dried at room temperature (<40 ºC) to constant mass before being divided and screened. The water content of the samples used for leaching was determined on a parallel sample by drying at 110ºC overnight. Moisture content was then determined in a special balance (Acculab L). Wet and dry density of samples was determined using ASTM D 4254 method. Samples' pH was determined using a Cyber Scan PC510 pH meter. The chemical composition of dried samples was determined by X-ray fluorescence (XRF, Phillips PW 2404). Mineralogical composition of previously calcined (at 1000 ºC) samples was determined by X-ray diffraction analysis (Bruker D4 Endeavor XRD). The acceleration voltage and current were 40kV and 30mA respectively. Leaching tests were performed according to EPA-1311 method (Toxicity Characteristic Leaching Procedure) to determine metals mobility under natural worst case conditions. The liquid/solid ratio was 20 L/kg. The mixture was stirred for an 18 hour period at a rate of 30±2 rpm and then filtered with a 0.7 µm filter. The pH of the mixtures were measured and decreased by adding nitric acid to be less than 2. After TCLP test, elemental (Cd, Co, Cr, Mn, Ni, Pb, V and Zn) concentrations were determined using atomic absorption spectrometry (Buck Scientific 210 VP model). The morphology of the waste samples was observed using a Research Polarize Microscope. A Zeiss RPM device was used and photography was taken by a Canon J5 scientific camera with size 150X. Photographs of samples were prepared by making a 30 µm thin section slid sample from the waste. The photography was taken with both reflected and transparent light methods.

## RESULTS & DISCUSSIONS

The physical characteristics of the samples are presented in Tables 1. Results show mean pH, wet and dry density and moisture content of the waste are 6.31, 1532 kg/m$^3$, 1879 kg/m$^3$ and 15.35 % respectively. The waste has an approximately high density in the dry form. Samples' mean pH shows a weak acidic condition dislike some other reported waste characteristics (Saikia, *et al.*, 2005) which may be related to the presence of high amounts of sulfur in the power plant studied waste.

**Table1. Physical characteristics of the waste samples**

| Sample Code | Moisture Content (%) | Wet Density ($kg/m^3$) | Dry Density ($kg/m^3$) | pH |
|---|---|---|---|---|
| 1 | 14.65 | 1502 | 1933 | 6.32 |
| 2 | 14.77 | 1565 | 1904 | 6.34 |
| 3 | 17.58 | 1546 | 1936 | 6.30 |
| 4 | 12.22 | 1593 | 1867 | 6.28 |
| 5 | 15.95 | 1488 | 1811 | 6.30 |
| 6 | 15.45 | 1597 | 1937 | 6.29 |
| 7 | 16.85 | 1434 | 1765 | 6.33 |
| Mean | 15.35 | 1532 | 1879 | 6.31 |
| Standard Deviation | 1.61 | 56 | 63 | 0.02 |

**Table2. Chemical composition of the thermal power plant air heater washing waste samples**

| Sample Code | 1 | 2 | 3 | 4 | 5 | 6 | 7 | Mean | Standard Deviation |
|---|---|---|---|---|---|---|---|---|---|
| Na2O(%) | 0.603 | 0.466 | 0.531 | 0.654 | 0.435 | 0.41 | 0.43 | 0.50 | 0.09 |
| MgO(%) | 2.731 | 1.528 | 1.71 | 1.465 | 1.348 | 1.83 | 1.73 | 1.76 | 0.42 |
| Al2O3(%) | 2.150 | 2.528 | 2.684 | 2.551 | 2.514 | 2.700 | 2.990 | 2.59 | 0.23 |
| SiO2(%) | 5.378 | 6.027 | 5.990 | 5.987 | 6.213 | 5.86 | 5.9 | 5.91 | 0.24 |
| P2O5(%) | 3.71 | 3.203 | 3.578 | 3.651 | 3.606 | 2.91 | 3.1 | 3.39 | 0.29 |
| Fe2O3(%) | 71.694 | 72.696 | 66.932 | 71.543 | 70.941 | 64.48 | 63.9 | 68.88 | 3.42 |
| MnO(%) | 0.450 | 0.346 | 0.502 | 0.323 | 0.359 | 0.590 | 0.680 | 0.46 | 0.12 |
| K2O(%) | 0.154 | 0.167 | 0.203 | 0.212 | 0.192 | 0.132 | 0.14 | 0.17 | 0.03 |
| CaO(%) | 2.251 | 2.717 | 2.897 | 2.590 | 2.919 | 2.520 | 2.57 | 2.64 | 0.21 |
| TiO2(%) | 0.07 | 0.081 | 0.07 | 0.093 | 0.083 | 0.07 | 0.08 | 0.08 | 0.01 |
| S(mg/kg) | 15700 | 16420 | 24900 | 20220 | 18450 | 16892 | 16864 | 18492 | 2960.43 |
| Cl(mg/kg) | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.00 |
| V(mg/kg) | 83220 | 56100 | 83640 | 54670 | 54920 | 59165 | 59173 | 64413 | 12145.13 |
| Ni(mg/kg) | 18970 | 18560 | 17280 | 18070 | 17780 | 15439 | 15529 | 17375 | 1296.16 |
| Zn(mg/kg) | 1930 | 1580 | 1510 | 1690 | 1600 | 1130 | 1140 | 1511 | 268.08 |
| Br(mg/kg) | 610 | 360 | 510 | 450 | 260 | 530 | 450 | 453 | 106.73 |
| Sr(mg/kg) | 530 | 750 | 660 | 690 | 790 | 485 | 487 | 627 | 117.06 |
| Cr(mg/kg) | 6213 | 6095 | 5979 | 5983 | 6004 | 6745 | 6633 | 6236 | 297.85 |
| Cd(mg/kg) | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 1 | 0.49 |
| Co(mg/kg) | 126 | 124 | 124 | 124 | 123 | 175 | 104 | 129 | 20.21 |
| Hg(mg/kg) | 1 | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0.45 |
| Pb(mg/kg) | 230 | 187 | 223 | 237 | 273 | 256 | 199 | 229 | 27.85 |
| Mo(mg/kg) | 4 | 4 | 4 | 4 | 4 | 220 | 10 | 36 | 75.26 |
| Ba(mg/kg) | 645 | 647 | 646 | 645 | 645 | 22 | 22 | 467 | 281.71 |
| As(mg/kg) | 7 | 7 | 8 | 7 | 7 | 7 | 7 | 7 | 0.35 |



Chemical composition of waste samples determined by XRF method is presented in Table 2. As we were concerned on the presence of heavy metals in this study, all the related components have been determined and presented. The results show that magnetite, $SiO_2$, $P_2O_5$, CaO, $Al_2O_3$ and MgO were the main constituents of the waste with the weigh percent order of 68.88, 5.91, 3.39, 2.64, 2.59 and 1.76% respectively. The main constituent of the waste is $Fe_2O_3$ that is confirmed by XRD results in Table 3. Percentile of $Fe_2O_3$ in Shahid Rajaee power plant waste is much higher than reported magnetite content of some other studied wastes such as fly ash, municipal solid waste, sewage sludge incinerator ashes and power plant ash and slag (Saikia, *et al.*, 2005; Oman *et al.*, 2002 Other main constituents of the waste (i.e. $P_2O_5$, (CaO, $SiO_2$, MgO and $Al_2O_3$) are in lower concentrations in comparison with other reported characterized wastes (Saikia, *et al.*, 2005; Li, *et al.*, 2004; Oman, *et al.*, 2002). Mean concentrations of some trace elements such as Cr, Ni, V and Zn fall in higher range that make them more noticeable, but some other elements such as As, Cd and Hg have lower concentrations. As it can be seen in Table 2, fuel oil related metals (V, Ni, Zn, Sr, Cr and Ba) are present in high concentrations in the waste. Higher mean concentrations of V, Ni, Zn and Cr (64413, 17375, 1511 and 6236 mg/kg respectively) and lower mean concentration of Cd and As (1 and 7 mg/kg) in the present studied waste than some other reported combustion residues waste is related to the origin of this waste that are fuel oil and corrosion products of air heater alloys and generation process of the waste. Some lighter elements such as Fe, Mn and Mg concentrations are quite high that seems to have a source other than the fuel residues in the waste. The other main source of these elements in the waste may be the heat transfer surfaces alloys corrosion products that would dissolve into the wastewater flow during the washing process. High content of some metals like Al and seems to be related to the use of alum and lime for coagulation/precipitation of air heater washing wastewater in effluent treatment plant.

**Table 3. Results of XRD of power plant waste amples**

| Sample Code | Description |
|---|---|
| 1 | AMORPHOUS + MAGNETITE |
| 2 | AMORPHOUS + MAGNETITE |
| 3 | AMORPHOUS + MAGNETITE |
| 4 | AMORPHOUS + MAGNETITE |
| 5 | AMORPHOUS + MAGNETITE |
| 6 | AMORPHOUS + MAGNETITE |
| 7 | AMORPHOUS + MAGNETITE |

## MORPHOLOGY

It is clear that the particle properties of the waste are linked to its leaching behavior. For example, the presence of non-porous continuous outer surface and dense particle interior may prevent heavy metal leachability from the ash. In this regard, the study of the morphology of the waste and its influence on the leachability of heavy metals could be of practical importance (Li, *et al.*, 2004; Ramesh and Kozinski, 2001). Figure 1 shows some photos from SEM photography of the natural waste. It can be seen that most of the sample has an amorphous texture. Some compounds of wet oxidized ferrous can be seen that are most likely $Fe_3O_4$, FeOOH or $Fe_2O_3+H_2O$ colored reddish dark brown and the spaces between them are filled with amorphous compounds and some crystallized siliceous and crypto crystal quartz material. We could also see two species of mono-cellular creatures in the photos that are probably caused because of the storage of the waste outdoor in a non-sheltered pit for some time.

## MINERALOGY

Mineralogy is the main way to understand the coalescent status of elements in the waste. Toxicity of the waste is dependent not only on the polluting elements concentration, but also on the specification of the pollutant elements and nature

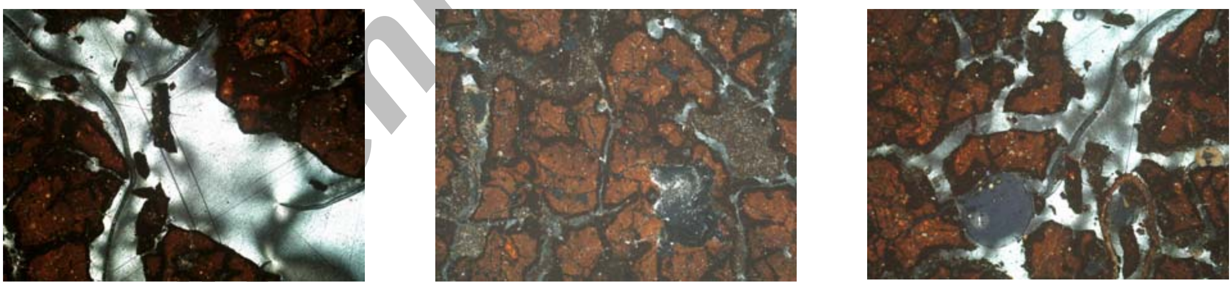

**Fig. 1. SEM photography of natural waste**

of the host phases (Forestier and Libourel, 1998). Table 3 shows the XRD analyses of the waste. As it could be seen in this table, the waste has an amorphous mineralogical structure with magnetite and as nearly most of the waste has an amorphous texture, there was no specific peak on the XRD graph.

## LEACHING CHARACTERISTICS

Different leaching tests have been developed to determine the interaction of wastes with the surrounding environment. For instance, leaching tests can provide a good insight into the mobility of heavy metals (Armesto and Merino, 1999). In addition, leaching tests play a major role to assess the possibility and use of treatment within regulatory limits (Ibanez, *et al.*, 2000). In this study the TCLP test has been used. The concentrations of studied heavy metals (Cd, Co, Cr, Mn, Ni, Pb, V and Zn) after TCLP test are presented in Table 4. Results showed that mean elemental concentrations of Cd, Co, Cr, Mn, Ni, Pb, V and Zn in leachate were 0.06, 1.55, 5.49, 36.32, 209.10, 0.58, 314.06 and 24.84 mg/lit respectively. Mean Cr concentration in leachate is higher than its EPA threshold leaching test concentration. Mean concentrations of Ni and V in leachate are also extremely high. This waste is subject to weathering, leaching and other natural processes during storage, disposal or utilization so contaminants can be leached from the waste and may be released to soil, groundwater and surface waters (Lopes, *et al.,* 2001).Therefore, regarding results of the TCLP tests studied waste can be classified as hazardous and should be disposed according to hazardous waste disposal considerations or should be stabilized before being disposed.

## CONCLUSION

For the first time in Iran waste from air heater washing wastewater treatment dewatered sludge of a thermal power plant were subjected to characterization studies through chemical composition, mineralogy, electron microscopy and TCLP leaching characteristics test. Results revealed that waste is weakly acidic with dry density of 1879 kg/m$^3$. Main chemical constituents of the waste were magnetite, $SiO_2$, $P_2O_5$, CaO, $Al_2O_3$ and MgO with 68.88% $Fe_2O_3$. Mean elemental concentrations of Cd, Co, Cr, Mn, Ni, Pb, V and Zn in waste leachate were 0.06, 1.55, 5.49, 36.32, 209.10, 0.58, 314.06 and 24.84 mg/L respectively. Regarding results of the TCLP tests, studied waste can be classified as hazardous and should be disposed according to hazardous waste disposal considerations or should be stabilized before being disposed.

**Table 4. Concentrations of heavy metals in leachate after TCLP test of studied waste**

| Sample Code | Concentration (mg/L) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Cd | Co | Cr | Mn | Ni | Pb | V | Zn |
| 1 | 0.07 | 1.28 | 5.59 | 35.52 | 204.72 | 0.48 | 311.20 | 25.00 |
| 2 | 0.08 | 1.77 | 5.69 | 34.86 | 200.84 | 0.62 | 309.60 | 27.50 |
| 3 | 0.06 | 1.77 | 5.41 | 36.38 | 211.49 | 0.65 | 315.70 | 24.96 |
| 4 | 0.06 | 1.67 | 5.40 | 36.91 | 211.06 | 0.47 | 314.10 | 23.25 |
| 5 | 0.05 | 1.52 | 5.50 | 37.46 | 211.69 | 0.70 | 310.50 | 23.24 |
| 6 | 0.05 | 1.43 | 5.00 | 37.54 | 214.95 | 0.64 | 316.80 | 23.08 |
| 7 | 0.05 | 1.40 | 5.86 | 35.54 | 208.95 | 0.53 | 320.50 | 26.85 |
| Mean | 0.06 | 1.55 | 5.49 | 36.32 | 209.10 | 0.58 | 314.06 | 24.84 |
| Standard Deviation | 0.01 | 0.18 | 0.25 | 0.96 | 4.44 | 0.08 | 3.63 | 1.66 |



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