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## Characterization of Thermal Power Plant Fuel Oil Combustion Residue

M. Saeedi and A.Rezaei Bazkiaei  
Environmental Research Laboratory,  
Department of Hydraulics and Environment, College of Civil Engineering,  
Iran University of Science and Technology,  
16846, Tehran, Iran

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**Abstract:** In the present study, physical properties, chemical composition and leaching properties of a special waste type; fuel oil combustion residue of thermal a power plant, have been studied. Toxicity Characteristic Leaching Procedure (TCLP), sequential chemical extraction (SCE), alkalinity solubility and release as a function of pH" leach tests and X-ray Diffraction (XRD) analysis have been employed to achieve a more comprehensive understanding of waste characteristics. Elemental V, Ni, Fe, Cr, Pb and Cd concentrations have been traced in leachates from different tests. Results have shown special characteristics such as; extremely low pH level about 2.7, high Sulphur content; 21.50 weight percent and elemental V complex formation in untreated material. Results of TCLP test have shown excessively high concentration of V, Ni, Fe, Cr, Pb and Cd in leachates as 537.75, 472.5, 518.5, 38.54, 19.3 and 5.55 mg L<sup>-1</sup>, respectively. Results of SCE test show Ni, Fe and Cr, are most likely to be present in residue fraction, Pb in exchangeable fraction, Cd in bound to iron and manganese oxides and V is most likely to be present in bound to organic matter and sulfides but also a considerable fraction of it resulted to be in bound to iron and manganese oxides. Results of alkalinity, solubility and release as a function of pH test show relatively same release change pattern for Ni and Fe in pH range 2 to 5, but release reduction in pH 6 for Fe has steeper pattern than Ni. For other constituents, release changes do not show such abrupt pattern with pH variation. According to TCLP test results, the studied waste should be classified as hazardous and should certainly be stabilized and then disposed of according to hazardous waste disposal considerations. Sequential chemical extraction and release as a function of pH tests have made useful insights of waste intrinsic characteristics that can help for a better decision on best remedial technology that matches the waste characteristics.

**Key words:** Fuel oil, combustion residue, TCLP, sequential chemical extraction, alkalinity solubility and release as function of pH

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## INTRODUCTION

Several studies on practical applications of pollution characterization have been done in different receptor environments and by means of different evaluation methods and practices such as: characterization of organic pollutants level in water, sediment and living marine organisms of system of a river delta (Chau, 2006, 2005) and characterization of thermal power plant and combustion residue waste types (Asokan *et al.*, 2005; Saeedi and Amini, 2006) to ascertain compliance with national and international risk and hazard regulations. More pointedly, real importance of waste characterization studies is in their essential aid to develop a more efficient stabilization method. The characterization of different stabilized and unstabilized waste materials has been studied by many

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**Corresponding Author:** M. Saeedi, Environmental Research Laboratory, Department of Hydraulics and Environment, College of Civil Engineering, Iran University of Science and Technology, 16846, Tehran, Iran

researchers from different points of view (Geysen *et al.*, 2004; Luz *et al.*, 2006; Saika *et al.*, 2006; Sophia and Swaminathan, 2005). Although the chemical composition and leaching characterization of heavy metal-containing residue-type waste materials have been studied before elsewhere, most of characterized waste materials are combustion residues of Municipal Solid Waste (MSW) incinerators (Bagnoli *et al.*, 2005; Eighmy, 1995; Forestier, 1998; Ibanez *et al.*, 2000; Jing *et al.*, 2006; Li *et al.*, 2004) or originated from coal-fired power plants (Armesto, 1999; Asokan *et al.*, 2005; Dincer *et al.*, 2006; Ilham *et al.*, 2001; Snigdha and Vidya, 2006; Lopes *et al.*, 2001) or from other sources in thermal power plants (Saeedi, 2006).

Due to the fact that fuel oil is a heavy carbon containing material, commonly called as heavy oils and can be used in many other industries like cosmetic and perfume production, this kind of material is not used for the purposes of heat production internationally, but in Iran, considering the fact that required processing facilities are not available for such intentions and most of electricity is generated by thermal power plants; fuel oil is used for heat production purpose in thermal power plants. Fuel oil is burnt to generate electricity in thermal power plants during late autumn and winter (Anonymous, 2005a). The most commonly fuel oil type used in Iran is Fuel oil-Redwood 2000. In almost all cases, fuel oil production procedure in refinery sites does not include any preplanned facility to completely purify existing impurities imposed to crude, thus sandy-loamy, silica and sulphur containing impurities are often observed in final products of refining towers (Anonymous, 2005c) that may lead to some special characteristics in combustion products. Fuel oil combustion residues in Iran's thermal power plants have not yet been characterized to ensure environmental regulations or to assess any possible alternatives for fuel oil utilization. Even if its usage just be limited to the cold seasons, this type of waste is classified as specific industrial waste, which regardless of quantity needs to be characterized in detail under the waste management act of Iran (Anonymous, 2005a). In the present investigation four composite samples of fuel oil combustion residue of Shahid Rajaei thermal power plant have been subjected to investigation of physical properties, chemical composition and leaching properties to assess its compatibility with Iran's hazard regulations. Shahid Rajaei thermal power plant is located 100 km west of Tehran, Iran's capital, consists four 250 MW, natural gas and fuel-oil-burning units.

## **MATERIALS AND METHODS**

In January 2006, 20 waste samples were taken from bottom ash of combustion tower of Shahid Rajaei power plant. The collected samples were stored in a cool place in sealed bags until analysis. Four composite samples were prepared by homogenizing and combining every fifth sample. The samples were air dried at room temperature (<40°C) to constant mass before being divided and screened. The water content of samples used for leaching was determined on a parallel sample by drying at 110°C overnight. Moisture content then was determined using ASTM 4254 (Anonymous, 2000) method. The natural pH of samples was determined using Cyber Scan PC510 pH meter. The chemical composition of dried samples was determined by X-ray Fluorescence (XRF) method and X-ray Diffraction (XRD) measurement was used to identify possible mineral phases in the waste sample.

Different leaching tests utilized for a comprehensive coverage of waste leaching characteristics:

- Toxicity Characteristic Leaching Procedure (TCLP) (Anonymous, 1992); a commonly used leaching procedure to identify waste characteristic under a specific supposed worst case field condition; Acetic acid as leachant in pH 2.88±0.05 over liquid to solid (L/S) ratio 20/1 and tumbling in an end-over-end fashion for period of 18 h.
- Sequential chemical extraction; according to Tessier *et al.* (1979); elements can be classified into the following five operationally defined fractions: 1) Exchangeable: the sample was extracted for

5 h with 0.5 M MgCl<sub>2</sub> at pH 7.0 and a L/S ratio of 8; 2) Bound to carbonates: the solid residual from step (1) was extracted with 1M NaAc at pH 5 and a L/S ratio of 8 for 5 h; 3) Bound to iron and manganese oxides: the residual from step (2) was extracted with 0.04 M NH<sub>2</sub>OH.HCl in 25% (v/v) HAc for 6 h at 96°C. The L/S ratio was 20; 4) Bound to organic matter and sulfides: the residual from step (3) was extracted with 30% H<sub>2</sub>O<sub>2</sub> for 6 h at 85°C, then extracted with 3.2 M NH<sub>4</sub>Ac in 20% (v/v) HNO<sub>3</sub> with continuous agitation for 30 min and (5) Residual: this fraction was calculated from digestion of remnant of step (4)

- Alkalinity solubility and release as a function of pH (Kosson *et al.*, 2002); The equivalents of acid or base are added to a combination of de-ionized (DI) water and the particle size reduced material (<2 mm), with Nitric acid solution 2N in situation where natural pH of samples is to be reduced or Potassium Hydroxide solution 2N where natural pH is to be raised, to cover desirable range of pH values which may occur under different field conditions, with final L/S ratio 10 in an end-over-end fashion for 24 h to identify leaching characteristics of samples over a broad range of possible pH value (2 to 12) and in fact more realistic conditions over different plausible management scenarios.

Performing the tests, elemental V, Ni, Fe, Cr, Pb and Cd concentrations of eluates from different tests were determined using atomic absorption spectrometry (Buck Scientific 210 VP model).

## RESULTS AND DISCUSSION

This study is the first waste characterization practice of this type in Iran which looks forward to assess the quality of a special thermal power plant waste product; fuel oil combustion residue. The results show mean moisture content, wet density, dry density and natural pH of the waste, these parameters amount to 2.02%, 1929.5, 1859.5 kg m<sup>-3</sup> and 2.71, respectively (Table 1). The waste obviously shows low pH level and high acidic condition that stands notably higher than many other thermal power plant originated wastes (Ilham *et al.*, 2001; Saeedi, 2006) which are usually nearly among 5 to 7 in the worst case. It must be noted that, this matter has caused some ephemeral harsh irritation effect on inspiratory system of researcher because of tiny particle smog arising during mixing and homogenizing procedure. From another point of view, water content of the waste is considerably low and its density is not excessively high. These factors may be considered as matters of notice if the waste type is to be used as secondary light material production, which may be a scope of research throughout future remediation and stabilization studies. Low water content of waste type is considered to be as an obstacle or at least a limiting factor in selection of possible recycling techniques for constituents of interest, because many of physical or chemical recycling technique are based on separation, precipitation or absorption of elements from aqueous phase to solid phase which may necessitate a pretreatment operation on waste in present relatively dry form.

The average chemical composition of four waste samples determined by XRF analysis shows LOI, SO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, Fe, Ni, Na<sub>2</sub>O, Cr<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CaO, Al<sub>2</sub>O<sub>3</sub>, MgO, K<sub>2</sub>O, PbO, MnO and TiO<sub>2</sub> are the

Table 1: Physical properties of four analytical samples of fuel oil combustion residue and average values

Sample code	Moisture content (%)	Wet density (kg m <sup>-3</sup> )	Dry density (kg m <sup>-3</sup> )	pH
1	1.85	1946.0	1898.0	2.65
2	2.11	1887.0	1852.0	2.81
3	1.95	1898.0	1833.0	2.68
4	2.18	1987.0	1855.0	2.70
Avg.	2.02	1929.5	1859.5	2.71

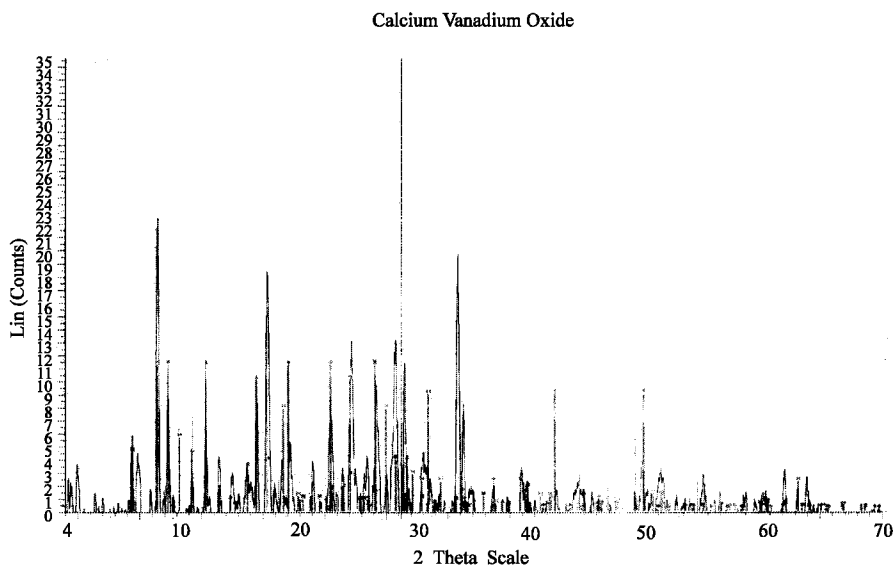


Fig. 1: Result of XRD analysis for final composite sample of fuel oil combustion residue waste

- File: 1764a.raw-Type: 2TH/ locked-Start:4.000-End 70.000-Step: 0.02 -StepTime: 1 35-0615(1)-Munirite-  
NaVO<sub>3</sub>·2H<sub>2</sub>O- Y:50%-d x by:1 Operations: Background 1.000,1.000
- 26-1165(1)- Calcium Vanadium Oxide-beta-Ca<sub>0.17</sub>V<sub>2</sub>O<sub>5</sub>-Y: 50%-d x by:1- WL: 1506.
- 39-1425(\*)- Cristobalite, Syn-SiO<sub>2</sub>- Y 50%- d x by:1-WL: 1.5436-Tetragonal-a 4.9732.
- 37-1496(\*)- Anhydrite, Syn- CaSO<sub>4</sub>- Y:50%- d x by:1-WL: 15406-Orthorhombic-a 6.9.
- 27-0950(1)- Vanady1 Sulfate Hydrate- VOSO<sub>4</sub>·3H<sub>2</sub>O- Y:50%- d x by:1-WL: 1.5406-Mon.
- 03-1209(D)- Iron Nickel- FeNi- Y:50%- d x by:-WL: 1.5460- Cubic-a 3.59100- b3.59
- 40-1115-Hydrogen Vanadium Oxide- H<sub>1.87</sub>V<sub>2</sub>O<sub>5</sub>- Y:50%- d x by:1WL:1.5406-1/c

main constituents of the waste on weight percentages basis in order of 36.76, 21.59, 17.12, 7.01, 6.02, 4.15, 2.07, 1.79, 1.53, 0.87, 0.3, 0.19, 0.14, 0.11 and 0.08, respectively and with detection limit of 0.05 weight percent. As it could be predictable due to formerly discussed possible impurities in fuel oil production process, high percentage of sulphur and silicium content is observed. This may strongly be contributed to probable sand, silica and sulphur impurities inserted due to oil extraction procedure (Anonymous, 2005c) and the accumulation process that may occurs in oil refineries and within the combustion unit. High percentage fraction of vanadium, nickel, chromium and lead in the waste material is also obviously notable. In a large majority of earlier studied wastes, which heavy metal concentrations have been in a considerable amount, elemental V has not even exceeded 1 weight percent fraction, similarly for the case of Ni and Cr, concentrations have not been reported more than about 2-3 weight percent in the literature and more often in concentrations below 1% (Asokan *et al.*, 2005; Dinceral *et al.*, 2006; Jing *et al.*, 2006; Saeedi, 2006). This may lead to future investigations on recycling potential of elemental V, Ni and Cr through different plausible and applicable techniques, specially for vanadium which its high concentration level interestingly provokes comprehensive studies on recycling opportunities. It seems that compared to many other studied residual waste forms such as: coal-fired thermal power plant bottom and fly ashes and MSW incineration residues, present investigated type of fuel oil combustion residue comparatively owns different characteristics, thus far.

Four homogenized samples were mixed together again to produce new composite sample for XRD analysis (Fig. 1). Result of XRD analysis which affirms metal complex formation in waste material. This must almost certainly be contributed to high temperature condition, about 1100-1500°C, in power plant combustion furnace that has made complex formation phenomenon possible. Regarding dominating phases, based on qualitative percentage present in the sample, major controlling complex

Table 2: Concentrations of constituents of interest in leachats of TCLP leach test for four samples in mg L<sup>-1</sup>

Sample code	V	Ni	Fe	Cr	Pb	Cd
1	540.65	485.6	525.6	34.8	25.5	5.85
2	525.36	455.6	530.8	37.8	13.5	5.12
3	536.85	478.9	505.7	41.06	19.6	5.99
4	548.65	469.8	512.6	40.5	18.6	5.25
Avg	537.75	472.5	518.5	38.54	19.3	5.55

Table 3: Results of SCE test, depicting percent of constituents of interest present in different predefined fractions in Tessier method

Percent of total element content %															
Fraction	V					Ni					Fe				
	S1	S2	S3	S4	Avg.	S1	S2	S3	S4	Avg.	S1	S2	S3	S4	Avg.
1	6.44	6.03	6.05	7.29	6.45	0.64	0.58	0.59	0.63	0.62	7.8	7.42	7.68	7.05	7.49
2	13.41	13.17	13.11	12.99	13.17	22.54	22.35	22.85	22.65	22.59	11.9	12.58	12.51	12.63	12.41
3	23.55	25.37	26.22	28.23	25.84	16.93	16.35	17.03	14.27	16.13	27.16	28.4	28.4	28.57	28.04
4	36.27	36.82	36.57	34.89	36.14	3.11	2.89	3	2.65	2.91	10.96	10.62	10.62	11.12	11.14
5	20.04	19.16	17.79	16.61	18.4	56.81	57.77	56.85	59.8	57.74	42.18	40.78	40.78	40.63	40.93
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Fraction	Cr					Pb					Cd				
	S1	S2	S3	S4	Avg.	S1	S2	S3	S4	Avg.	S1	S2	S3	S4	Avg.
1	9.73	9.98	10.08	9.67	9.73	57.41	60.42	57.88	56.63	57.41	22.15	24.35	25.77	24.53	24.2
2	12.04	11.08	12.9	11.65	12.04	6.43	5.14	5.29	6.94	6.43	11.44	9.22	10.65	11.22	10.63
3	11.7	12.64	11.29	11.29	11.7	7.46	7.8	6.95	7.63	7.46	44.55	48.19	43.86	38.3	43.72
4	11.5	12.1	12.43	12.43	11.5	3.9	3.88	3.61	4.41	3.9	15.7	12.59	11.22	15.01	13.63
5	55.03	54.2	54.96	54.96	55.03	24.8	22.76	26.26	24.4	24.8	6.15	5.66	8.51	10.93	7.81
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100

S<sub>i</sub>: sample code (i: 1 to 4)

phase is concluded to be Calcium Vanadium Oxide (CaO.17V<sub>2</sub>O<sub>5</sub>) and minor one, Vanadyl Sulphate Hydrate (VOSO<sub>4</sub>.3H<sub>2</sub>O) based on XRD analysis result.

Results of TCLP leaching test are presented in Table 2. Concentrations of constituents of interest in leachats are too much higher than standard limits for TCLP test (Anonymous, 1992).

Results of SCE test, presented in Table 3, show that Ni, Fe and Cr, are most likely to be present in residue fraction, whereas fraction percent for step 5 is 57.74, 40.93 and 55.03% of total, respectively which stands for the biggest portion of fractions for mentioned elements; Cr has shown a considerable percent of about 22% for two first fractions that still stands for a large leachable portion of Cr that can readily leach to ambient environment (Table 3). Pb is most likely to be present in exchangeable fraction due to its highest percent contributed to first step, 57.41% and Cd in bound to iron and manganese oxides due to its highest percent in fraction 3, 43.72%, but obviously there exist a large portion of these two hazardous elements in first two fractions; 64 and 34%, which should stand as a dramatic point of notice in future supposed stabilization processes. V is most likely to be present in bound to organic matter and sulfides due its higher percent in this fraction; 36.14% but also a considerable percent of 25.84% is resulted to be in bound to iron and manganese oxides, high percent of Fe reported in XRF analysis affirms high concentration of Fe present in samples and possible bounds to Fe oxides, while XRD result shows vanadium complex formation with Sulphure and Calcium in oxide form as well.

Results of alkalinity, solubility and release as a function of pH (Table 4). Amount of constituent's concentration in leachate for pH ranges between 2 to 12 are presented. According to observed pattern of release changes, generally, it is obvious that all constituents show excessively high release amounts on a wide range of pH values and release is reduced with increase in pH for all constituents of interest, but there are some different change rates at different pH values. For Ni and Fe, leaching in range pH 2 to 5 has relatively same change pattern but release reduction in pH 6 for Fe

Table 4: Concentration of constituents of interest in alkalinity, solubility and release as a function of pH test for different pH values in mgL<sup>-1</sup>

pH	mg L <sup>-1</sup>				
	Ni	Fe	Cr	Pb	Cd
2	325.28	495.56	84.53	19.5	2.1
3	311.15	395.68	79.22	18.68	1.97
4	258.65	233.36	14.85	17.56	1.59
5	212.30	111.37	9.95	17.22	1.51
6	178.65	34.15	6.27	10.65	1.17
7	105.32	25.50	5.32	9.67	1.42
8	100.25	18.90	4.65	6.32	1.37
9	96.65	15.56	3.93	5.68	0.95
10	76.38	13.90	3.58	3.22	0.82
11	68.33	10.57	3.53	3.17	0.72
12	55.58	8.92	1.96	2.65	0.38

has steeper pattern than Ni. For other constituents, release changes do not show such abrupt pattern with pH variation. Relatively high changes in released amounts in different pH levels must be considered as a good representative of real field conditions which may lead to a more efficient stabilization method with less operational costs. For example in a supposed site land filling of raw waste material or even stabilized waste, real alkaline condition of surrounding soil must be evaluated to assess real potential of acid attack to the dumped materials and leaching potential of metallic elements as long term environmental condition of final dump site. This may lead to a not over-designed stabilization scheme, with fair consideration of real site-specific conditions and finally in lower operational costs in field. As stated in Kosson investigation (Kosson *et al.*, 2002) on evaluation of waste materials from the view point of real site-specific condition of management scenario, just considering TCLP leach test standard criteria as adequate characteristic of violation from hazard standards, is one of the most critical criticisms have been done to TCLP leach test.

## CONCLUSION

In the present investigation, first of this type in Iran, four composite samples of fuel oil combustion residue of thermal power plant, as a special waste, have been subjected to investigation of physical properties, chemical composition and leaching properties. Use of fuel oil for heat production purposes in thermal power plants is by itself a unique feature of this study.

Results show that this waste material owns special characteristics resorted as follows; high acidic condition, high percentage of S, V, Ni, Cr and Si in untreated material and dramatically high release amounts of constituents of interest in different test methods upper than health and hazard limits. According to TCLP test results, the studied waste should be classified as hazardous and should certainly be stabilized and then disposed of according to hazardous waste disposal considerations. Sequential chemical extraction and alkalinity, solubility and release as a function of pH tests have made useful insights of waste intrinsic characteristics that can help for a better decision on best remedial technology that matches the waste characteristics.

More pointedly, with reasonable attention to specific characteristics of waste material, remedial options with final dump destinations may be the last options. In fact, comparison of different plausible waste management scenarios and on the other hand; assessment of potential recycling methods with regard to volume of waste generated each year must be done in parallel. Different possible physical and chemical recycling methods, waste management scenarios and their operational costs for elements with considerable concentration levels have not been investigated in the present study; this may be an open area of study for future investigations.

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