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Fly ash generated from heavy fuel incineration in power plants: Physical and chemical characteristics

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ABSTRACT

In Jordan, large amounts of fly ash (FA) are produced as a result of burning heavy fuel in power plants. The brackish granular flash ash was systematically analysed by different analytical techniques including scanning electron microscope (SEM), X-ray diffractometer (XRD), X-ray fluorescence (XRF). Fourier transform infrared spectroscopy (FTIR), lazier diffractometer (LD), Thermal gravimetric analysis (TGA) and acoustic and electroacoustic spectrometer in order to investigate geometrical structure, morphology, surface chemistry and composition of the resulted FA. The FA was sampled form the places where heavy fuel is burned to produce electricity. This study revealed that about 50% of FA particles diameters were less than 530 nm. FA particles were predominantly appeared as smooth of mineral spheres. The FA was rich in C, S, Mg, V, Ni and Fe indicating the carbonaceous nature of this material. The Al and Si contents were insignificant. The size distribution, chemical and morphological properties of the FA particles were found to be log-normal. The FA contains high heavy metals content, particularly vanadium oxide (V_2O_5: 8.07 %wt) and nickel oxide (NiO: 0.91 %wt). Discussion on the physical and chemical characteristics of carbonaceous FA produced in power plants is addressed in this work.

KEYWORDS

Fly ash;
Thermal power plants;
Heavy fuels;
Heavy metals;
Jordan;
Petroleum.

INTRODUCTION

In Jordan, the total power produced by Central Electricity Generating Company (CEGC) in 2010 was approximately 7660 GWh[1]. Heavy fuel, diesel and natural gas are the main sources for generating electricity in Jordan[1]. Diesel (average molecular formula $C_{12}H_{23}$) is highly consumed to generate electricity with a total amount of 68,000 m^3 in 2010[1]. On the other hand, the consumed amounts of heavy fuel and natural gas (mainly methane) were 837,000 ton and $1.84 \times 10^8 m^3$, respectively in 2010[1]. The combustion of heavy

fuel or diesel by excess oxygen is presented as: $4C_{12}H_{23} + 71O_2 \rightarrow 48CO_2 + 46H_2O$. However, in real situation, complete combustion of fuel is not possible and the incomplete combustion will come out with mixture of substances known as fly ash (FA)[2]. The large consumption of heavy fuel and diesel in power stations leaves about 420 ton of FA[3] and this number is expected to increase dramatically in the following years due to the natural growth rate of energy demand and shortage of natural gas supplying.

In terms of resource recovery and environmental impact, FA is attracting much attention due to disposing problems and its harmful impact on the soil because of metal leaching[4,5]. In fact, research on this topic is rather limited and indicated that FA produced in heavy fuel power stations is rich in Ni, V, Fe, Mo, Mg, Na and C and among these metals Ni and V are the most valuable[4,5]. Accordingly, FA would be a source of pollution due to metal leaching and in the same time it is commercially attractive due to the presence of high levels of V and Ni.

Currently, Jordan is heading to use oil shale as a major source of energy. Oil shale-fuelled power station is a proposed project to build in Jordan. The power station is expected to be operational by 2015. It would be one of the largest power stations in the world after Narva Power Plants in Estonia. Accordingly, a huge amount of FA will be produced as by-product. A visionary scenario of using this kind of FA as metals recovery and cement geo-polymer were fully investigated.

Traditionally all electric power in Jordan has been generated from heavy fuel oil. However, the dramatically increasing of oil price and establishing the Egyptian gas pipeline with reasonable price forced the Jordanian government to diversify its sources of power. In Jordan, there are 18 power stations, where two wind power station in Hofa and Ibrahhimya plant, two hydro power stations (king Talal Dame and Aqaba) as well as one Bio gas power station in al Russiefa. The rest number of power stations is working based on Natural Gas / Heavy fuel / Diesel. The major generated electric power has been based on the stations represented in TABLE 1.

TABLE 1 : Existing generation capacity[3]

Power plant	Type	Energy generating capacity MW	Fuel type
Aqaba	Steam / hydraulic turbines	650 / 6	Heavy fuel / Natural Gas
Hashemite	Steam / Gas turbine	363 / 33	Heavy fuel / Diesel
Samra	Steam / Gas turbine	300 / 200	Natural Gas
Rehab	Combined-cycle gas turbine / Gas urbine	300 / 60	Natural Gas
Amman East	Gas turbine	248	Natural Gas
Amman South G.T	Gas turbine	60	Natural Gas
Al-Qatrana	Gas turbine	373	Natural Gas
Risha	Gas turbine	150	Natural Gas / Diesel
Others	Steam turbines / Gas turbine	60	Natural Gas / Diesel / wind / Hydro

*[3]

The total consumed power in 2009 was approximately 3.44 million toe compared to 3.03 million toe in 2008 with a growth of 4.8%, this amount represented what is a proximately 45.1% of the total power consumption in Jordan by the primary energy in this year. The consumed natural gas magnitude has also reached 3090 thousand toes, the heavy fuel oil 261 thousand toes and 18 thousand kilo toe for diesel[3]. Based on the Jordanian Standard specification (2005)[6] and the international standard specification (2001)[7] for petroleum and petroleum products - fuel oil / ash residue, the estimated amount of produced FA in the year 2009 is 418.5 ton. This number is expected to increase dramatically in the year 2012 due to growth rate of energy demand and shortage of natural gas supplying. The biggest electric power station in Jordan (Aqaba thermal power station) converted completely to use heavy fuel instead of natural gas since March 27, 2011 because of explosion of a natural gas pipeline in Egypt.

Re-usage or recycle of FA can eliminate the cost of final disposal and prevent secondary pollution caused by inappropriate FA disposal. This fact, however, stimulates our awareness to investigate and characterise the petroleum FA which produced in Jordanian electrical

power stations for its chemical and physical properties. This is expected to add value to the future use of the FA recycle or application in Jordan.

Based on our earlier research on the FA[8], the material was found to be a good source for V and Ni and would be used in geopolymer fabrication and this is a safe way of reducing potential risk of FA. Worldwide, there are numerous examples of economically beneficial of FA utilisation and the situation in the world seems to us to be another promising case. However, complete characterisation, detailed spectral and chemical analyses of the FA produced in our power stations are carried out in this paper.

MATERIALS AND METHODS

Collection of the FA samples

The FA was collected from Central Electricity Generating Company, Hussein Thermal Power Station of Jordan. The samples were directly taken from the places where heavy fuel is burned to produce electricity. The ash was collected as course particles and used as received without any physical treatment. About 2 kg of the FA was collected on different occasions. All collected samples were mixed and the final mixture was used to carry out extraction experiments. The ash has a black colour with density of 0.42 g/cm^3 which is similar to that of activated carbon. The textural properties of the ash was evaluated by doing scanning electron microscopy, the material was pictured at high magnification power.

Characterisation of the FA

Geometrical size and shape of any solid material are important properties which would be tested using scanning electron microscope (SEM, FEI Company Inspect F50/FEG (Schottky Field Gun) High Vacuum (6e-4 Pa Everhart-Thornley SE detector Solid-State BSED), Netherland). A laser diffractometer (Microtrac Zetatrac, Microtrac S 3000/S 3500 series Particle Size Analyzer, USA) was used to measure the size distribution of the FA particles. The zeta potential was determined by an electroacoustic method using an acoustic and electroacoustic spectrometer (Microtrac Zetatrac, Microtrac S 3000/S 3500, USA). The surface charge (Q) of the FA particles was characterised by a zeta potential (ζ) measurement. Zeta potential is a measure of the electrostatic potential generated by accumulation of ions that are organised into an electrical double-layer at the surface of a particle[9]. The zeta potential determines the colloidal stability[10], as given in the equation:

$$Q = 4\pi\varepsilon\varepsilon_0\zeta r(1+\kappa r) \quad (1)$$

where ε is the relative dielectric constant of medium, ε_0 is the dielectric constant of vacuum and κr is the electrokinetic radius. Surface area and porosity were investigated by N_2 gas adsorption theories using Micromeritics instrument, Gemini VII, USA. The accumulated gas quantity adsorbed versus gas pressure data at one temperature are then graphed to generate what is called an adsorption isotherm. The data are then treated to arrive at a specific surface area and porosity[11].

The total organic content (TOC) was determined using ELTRA CW multiphase CO_2/ H_2O determinator PC controlled from Germany. Thermal gravimetric analysis (TGA) (ELTRA Analyzers model TGA 701, LECO-USA) was employed to monitor the degradation behaviour of the FA particles. The sample was heated at a heating rate of 10°C min^{-1} in N_2 atmosphere.

X-ray powder diffraction (XRD) patterns were recorded using Cu Kα radiation source on a Scintag X1 powder diffractometer (Shimadzu X-Ray Diffractometer XRD-6000, Japan). The chemical composition of the FA was determined by X-ray fluorescence analysis measurements using a sequential X-ray spectrometer (Shimadzu XRF-1800 Sequential X-Ray Fluorescence Spectrometer, Japan).

RESULTS AND DISCUSSION

The main source of the chemical elements in the FA is the heavy fuel. The chemical composition of the FA raw material is presented in TABLE 2. The FA contains high heavy metals content, particularly vanadium oxide (V_2O_5: 8.07 %wt) and nickel oxide (NiO: 0.91 %wt). Magnesium oxide content is very high this is due to addition of magnesium hydroxide as additive to the heavy fuel (fouling agent). Power generating plants are reported to have chronic corrosion problems causing unscheduled shut-downs and frequent replacement of equipment and parts resulting in high maintenance costs and loss of production besides creating environment

problems. In an attempt to eliminate boiler internal corrosion and to reduce the hazardous nature of the flue gases Mg $(OH)_2$ as chemical fuel additives were used[12]. Studies on FA from Belgian coal sources indicated that chlorine, zinc, copper, silver, selenium, bromine, antimony and iodine were enriched in the FA relative to the source coal[13].

In comparison with FA produced by combustion of coal or oil shale, the FA in the present study has very low content of SiO_2, Al_2O_3 and Fe_2O_3. The standard chemical requirements of ASTM C 618 (2005)[14] include the sum of SiO_2, Al_2O_3 and Fe_2O_3 content must be ≥70% for class F and ≥50% for class C. The total carbon content was 34.60 wt%. Bayat (1998)[15] reported that the Al_2O_3 + SiO_2 contents for Turkish FA were higher than 65 wt% for all samples and the LOI ranged from 1.33 to 6.47 wt% for all samples investigated. In the present study the LOI is 37%.

TABLE 2 : Chemical composition of raw fly ash

Major oxides	%wt	Trace elements	Ppm
MgO	13.12	V	30667
Al_2O_3	0.52	Ni	7125
SiO_2	0.86	Mo	85
CaO	0.80	Cd	< 0.1
Na_2O	3.24	Cr	146
K_2O	0.13	Zn	247
FeO	4.38	Cu	92.5
Total C	34.60	Pb	76.5
Total organic C	30.88		
Moisture content	2.63		
LOI	37.23		

Studying the textural and chemical properties of the FA is an important issue because it gives an idea about the final industrial application of this material including adsorbent, filler, fly ash, soil improver and geopolymers. Based on laser diffractometer (LD) results, the particle size distribution was log-normal Figure 1. It revealed that 50% of the FA particles diameters were < 530 nm. The operating conditions of the LD software are strictly valid for spheres or the particles adopt preferential orientations in the measurement cell. LD considers the measured diameter of any particle as the diameter of a sphere even if the particle is a rod, ellipse or irregularly shape[16,17].

These results disagree with those found by Bayat (1998)[15], Townsend and Hodgson (1979)[18], who reported the range of fine sand, silt and clay fractions in Turkish and British coal ash samples. This variation in size distribution is probably due to the different methods of the FA collection, used at the power stations and parent materials of the FA such as oils shale, coal or fuel.

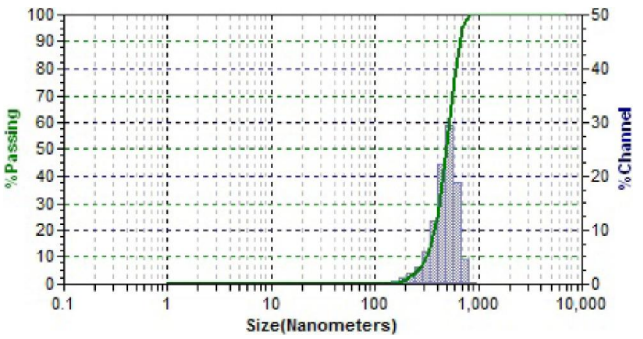

Figure 1 : Particle size distribution of the FA

The zeta potential measurements indicated that the surface of the produced FA was positively charged at pH > 1.5 (Figure 2). At pH 10, the zeta potential of the FA was 17.9 mV. However, the point at which the graph passed through zero potential was not attainable. For the FA particles, extrapolation of the zeta potential measurements using polynomial third order curves gave an estimated point of zero charge (PZC) at pH of 1.5. At PZC, the colloidal system exhibits zero zeta potential (i.e., the particles remain stationary in an electric field), minimum stability. The high negative or positive values of the zeta potential led to a stable suspension, which allows measuring the zeta potentials over a wide range of pH.

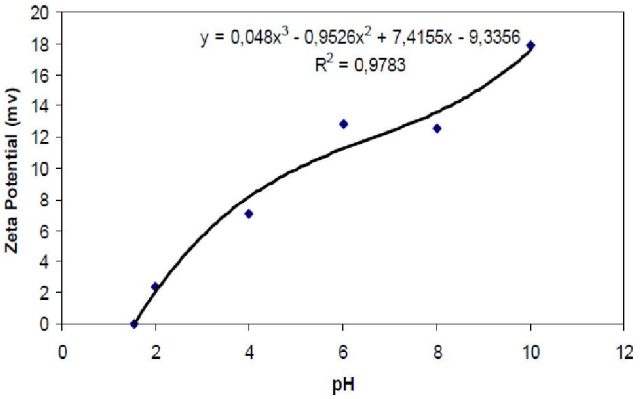

Figure 2 : Zeta potential of fly ash. Polynomial third-order curves were fitted to the data points

The FA is positively charged particles that would attract negatively charged ions or molecules within the

porous structure. According to the classification scheme of Riddick (1968)[19], the stability of the FA particles was low at pH > 9. The suspension stability was very bad at pH values less than 9, where the zeta potential is less than 15 mV. At low pH the particles stuck together in suspension and eventually formed agglomerates. According to Rumpf (1962)[20], the two forces influencing agglomeration of particles in solution are Van-der-Waals force and the repulsive force. The latter is strongly depending on ionic strength and zeta potential. The Van-der-Waals force increases with decreasing grain size[16,21]. The point of zero charge (PZC) was not attained because the suspension was not stable at pH < 2. This observation is in agreement with the estimated point of zero charge of pH 1.5. PZC is the pH value at which the net total particle charge becomes zero. At this pH value, particles do not move in an applied electrical field (electrophoretic mobility measurement)[9]. At PZC, the suspension is unstable because the Van-der-Waals force is higher than the repulsive force. The zeta potential strongly influences the ability of water or liquid to carry the FA particles in suspension. The FA pH was 2.6 at FA:water ratio 1:5. Bayat (1998)[15] reported values for pH of Turkish coal FA ranging from 9.5 to 12.5. This high pH value could be explained as a result of lime high content in the Turkish coal fly ash.

The surface property of the FA was characterised by FTIR spectroscopy, X-ray and SEM. An FTIR spectrum is shown in Figure 1 and XRD pattern is shown in Figure 2. The main FITR bands were: 3743, 1652, 1465, and 672 cm^{-1}. The bands at 1652 and 1465 cm^{-1} are attributed to vibrational frequencies of carboxylic acid group. The FTIR bands for metals were not detected and this would be attributed to the low content of the metals compare to carbon atom. It seems that the FA has a crystalline structure and this is inferred from the X-ray peaks in Figure 2. In fact, both FTIR and XRD results indicated the crystalline nature of the FA. The crystallinity ranges were between 85 and 100%. The obtained 2θ values were close to those reported for FA produced in power stations[22]. The X-ray results also confirmed that the FA was rich with carbon and sulphate with 80-88% by mass. The X-ray diffractogram patterns revealed that the mineral content of the FA particles is carbon, magnesium oxide, and magnesium vanadium oxide as well as sulphate minerals (Figure 4).

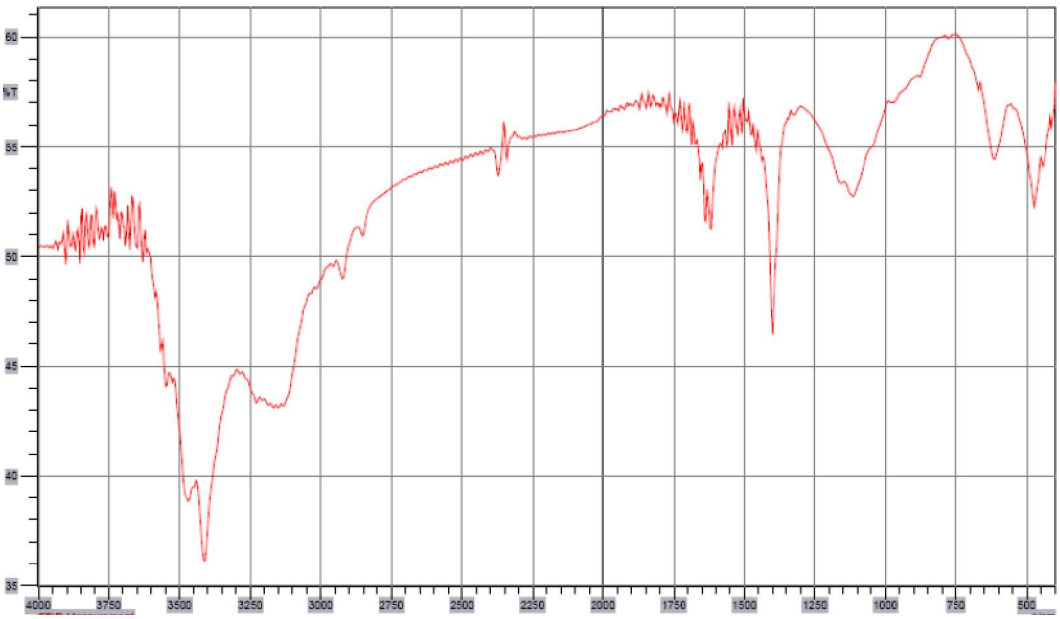

Figure 3 : FTIR spectra of the FA

SEM images revealed that the FA particles are almost totally spherical to semi spherical in shape, allowing them to flow and blend freely in mixtures (Figure 5). The spherical shape of the FA results from the formation of tiny molten droplets as the ash travels through the boiler. The droplets form spheres because this shape minimises the surface area relative to the volume. The SEM of the FA was also recorded at large magnification power to view the nature of the ash surface. In fact, the surface has many pores which created at high

burning temperature. Such porosity would be useful for other industrial application for the FA. In fact, this high porosity would facilitate the metals extraction. The large porosity is expected due to high temperatures accompanying fuel burning. Similar SEMs are reported in the literature[23,24].

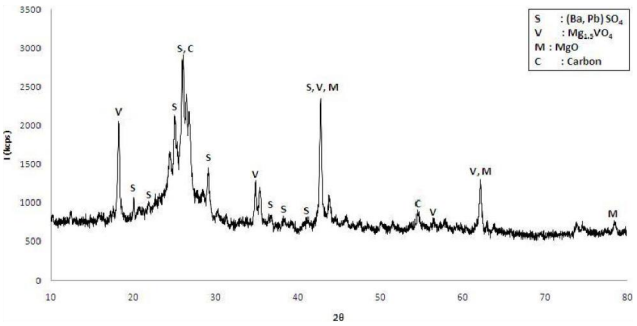

Figure 4 : X-ray diffractometer patterns of the FA

SEM imaging showed that the shape of larger FA particles tended to be irregularly with smooth edges and wavy grain boundary. The smaller particles were more spherical.

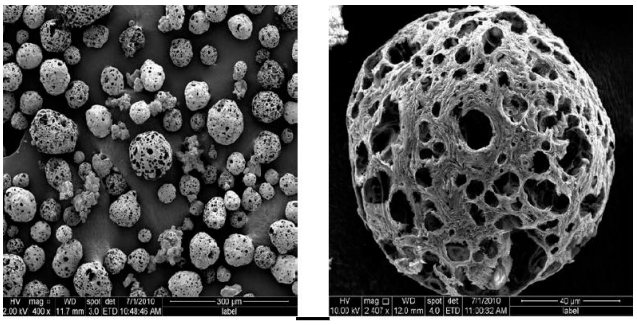

Figure 5 : SEM for fly ash sample at various magnifications

Nitrogen adsorption isotherm is shown in Figure 6. The isotherms are similar to type IV isotherms with a steep adsorption step at a relative pressure of 0.9. The specific surface area was determined by the Brunauer-Emmett-Teller (BET) method. The specific BET surface area of the FA collected from electrical power station was found to be 3.0 m^2 g^{-1}. The BJH (Barret-Joyner-Halenda) method was applied to analyse the mesopore size distributions using the adsorption branch. BJH Adsorption cumulative volume of pores is 0.016775 cm^3 g^{-1}. Pore Size Adsorption average pore width (4V/A by BET): 221.6847 Å.

TGA analysis was employed to monitor the degradation behaviour of the FA. Notable weight loss of approximately 32.8 wt% (Figure 7) is observed in the temperature range of 150~890°C which represents the degradation of organic and inorganic compound at temperature range (150 - 550°C) and (550 - 890°C), respectively. The moisture content is 2.6 wt% at 110°C The ash content at 800°C is 51 wt% as well as the fixed carbon is 13.3 dry wt%.

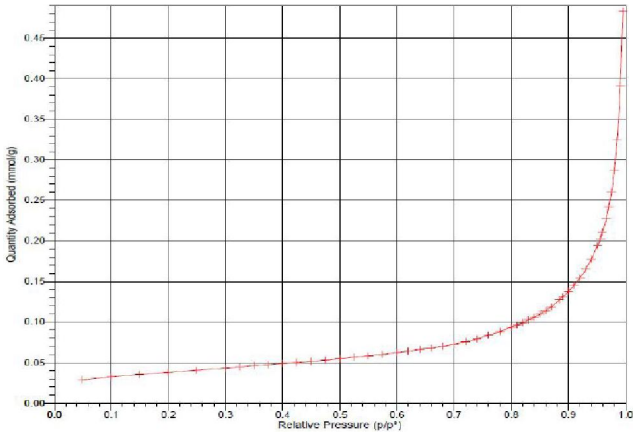

Figure 6 : Nitrogen adsorption isotherm for the FA particles

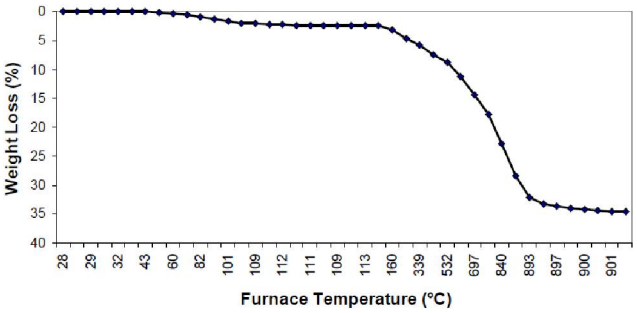

Figure 7 : TGA thermograms of the FA particles

CONCLUSIONS AND OUTLOOK

In Jordan, huge amounts of the FA are produced and even more production is expected in future. The perfect ways of utilizsing this material is still under investigation, however, extraction of expensive elements like (V & Ni) and application in geopolymers are being tested by us.

Knowledge of the physical and chemical properties of the FA is necessary for identifying and preventing problems concerning health, the environment. The present study characterised and described the FA that generated in petroleum heavy fuels-fired power plants. The FA is rich in V, Ni and Mg. The chemical and mineralogical compositions of Jordanian FA reflected the wide industrial application of this by-product.

The FA demonstrated a positive surface charge. By increasing pH the zeta potential increases. Based

on the surface chemistry and the surface positive charge over wide range of pH, Jordanian FA has high capacity to act as adsorbent for anions from solution. The FA has also a potential use in wastewater treatment. It has also the capacity of being used as an amendment for alkaline soil capable of improving soil conditions particularly, pH and the bioavailability of the essential elements for plants.

In conclusion, future investigations are also needed on the applicability and efficiency of this material for soil remediation purposes under field conditions. We encourage focusing scientific interest on metal recovery, geo-polymer and wastewater treatment as well as the ecotoxicity of Jordanian fly ash.

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REFERENCES

[1] **(a)** M.Steveson, K.Sagoe-Crentsil; J.Mater.Sci., **40**, 2023-2036 **(2005)**; **(b)** Central electricity generating company, The Hashemite Kingdome of Jordan, Annual Report, **(2010)**.
[2] M.A.Abdel-latif; Miner.Eng., **15**, 953-961 **(2002)**.
[3] Electricity regulatory commission. The Hashemite Kingdome of Jordan, Annual Report, **(2009)**.
[4] S.Vitolo, M.Seggiani, S.Filipi, C.Brocchini; Hydrometallurgy, **57**, 141-149 **(2000)**.
[5] S.Akita, T.Maeda, H.Takeuchi; J.Chem.Technol. Biotechnol., **62**, 345-350 **(1995)**.
[6] Jordanian standard specification for petroleum and petroleum products - fuel oil / ash residue, JS, 196 **(2005)**.
[7] The international standard specification. For products - determination of ash. ISO 6245, **(2001)**.
[8] Mohammad A.Al-Ghouti, Yahya S.Al-Degs, Ayoup Ghrair, Hani Khoury, Mahmoud Ziedan; Chemical Engineering Journal, **173**, 191-197 **(2011)**.
[9] G.Sposito; The chemistry of soils. Oxford University Press, New York, **(1989)**.
[10] A.Fernández-Nieves, F.J.Delas Nieves; Colloids and aurfaces A: Physicochemical and Engineering Aspects, **148(3)**, 231–243 **(1999)**.
[11] A.W.Paul, O.R.R.Clyde; Analytical methods in fine particle technology. 1st Edition, Second printing, Micromeritics Instrument Corporation, USA, ISBN 0-9656783-0-X, **(1997)**.
[12] P.C.M.Kutty, A.G.Dalvi, M.A.F.Al-Ghamdi, A.Hodan, A.Daghustani; Evaluation of chemical fuel additives to control corrosion and emissions in dual DUAL purpose desal/power plants. IDA conference, Abu Dhabi, 18-24 Nov, **(1995)**.
[13] C.Block, R.Dams; Environ.Sci.Technol., **9**, 146 **(1975)**.
[14] ASTM international standard, ASTM C 618. Standard specification for coal fly ash and raw or calcined natural pozzolona for use in concrete, **(2005)**.
[15] O.Bayat; Fuel, **77**, 1059-1066 **(1998)**.
[16] A.M.Ghrair, J.Ingwersen, T.Streck; Water Air Soil Poll., **203**, 155-168 **(2009)**.
[17] A.M.Ghrair; Immobilization of heavy metals in soil by amendment of nanoparticulate zeolitic tuff. Stuttgart: Univ. Hohenheim, Inst. für Bodenkunde und Standortslehre. - V, 103 S. : graph. Darst. - (Hohenheimer bodenkundliche Hefte ; 90). Hohenheim, Univ., Diss., **(2009)**.
[18] W.N.Townsend, D.R.Hodgson; In ecology and reclamation of devastated land, Gordon and Breach, New York, **1**, 45-56 **(1973)**.
[19] T.Riddick; Control of colloid stability through zeta potential; with a closing chapter on its relationship to cardiovascular disease. Published for ZETA–METER, INC. by Livingston Publishing Company, Wynnewood, Pennsylvania, 372 **(1968)**.
[20] H.Rumpf; The strength of granules and agglomerates, In: W.Knepper (Ed); Agglomeration. John Wiley & Sons, New York, 281-304 **(1962)**.
[21] T.Brar; Novel ways of synthesizing zeolite A. Master Thesis, The University of Cincinnati, Kharagpur, **(2000)**.
[22] G.Gupta, N.Torres; Use of fly ash in reducing toxicity of and heavy metals in wastewater effluent. Original Research Article. Journal of Hazardous Materials, **57**, 243-248 **(1998)**.
[23] Z.Sarbak, A.Sta Czyk, M.Kramer-Wachowiak; Powder Technology, **145**, 82-87 **(2004)**.
[24] S.Wang, L.Baxter, F.Fonseca; Fuel, **87**, 372-379 **(2008)**.