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Characterisation of Jarosite, Fly Ash and Clay for their possible usage in the construction industry

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Abstract -In this paper, the mineralogical and physical characterisation of Jarosite, Clay and Fly ash was investigated. The XRD results revealed the presence of alacranite (AsS) and jarosite (K ($Fe_3(SO_4)_2(OH)_6$)) mineral phases in the hazardous jarosite, while clay was composed of Kaolinite ($Al_2Si_2O_5(OH)_4$), Anatase (TiO_2) and Quartz (SiO_2). Furthermore, Fly ash contained phases Mullite ($Al_{4.64}Si_{1.36}O_{9.68}$), Quartz ($SiO_2$) and Calcium oxide silicate chloride ($Ca_2O_2Si_3Cl_2$). The XRF results confirmed that the Fly ash used is in class F (Hazardous material) . There were hazardous elements such as As and Pb in the Jarosite sample. Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM/EDS) revealed differences in surfaces morphology and EDS results were in agreement with the XRF analysis. The densities of the samples were 3.13 g/cm^3 , 2.67 g/cm^3 and 2.21 g/cm^3 for Jarosite, clay and Fly ash respectively. There was an increase in density with the increase of the percentage of Jarosite in the mixture whereas a decrease in density was noticed with the increase of Fly ash percentage in the mixture of Jarosite and clay.

***Keywords*:** Characterisation, Clay, Construction, Fly-Ash, Jarosite

1. Introduction

Since 1968, Impala Platinum Refineries (Implats) has been in the mining, beneficiation and marketing business of the PGMs together with cobalt, copper and nickel. Implats are the second largest producer of PGMs worldwide with two operating mines in South Africa. During the beneficiation process at the refinery, great amount of wastes are produced in liquid and solid form. Among the solid wastes being produced is hazardous jarosite (Impala Platinum Refineries waste streams, 2012).
Approximately 913 t/a of jarosite wastes are produced daily from the refinery where iron is precipitated using ammonium (NH_4^-) to form ammoniumjarosite $(NH)_4Fe_3(SO_4)_2(OH)_6$. Jarosite contains high amount of Iron and smaller quantities of Al, As, Ni, Pb, K, Co, Si etc. Due to the present of toxic elements such as Fe, As, Ni and Pb, jarosite is considered hazardous to the environment as it can pollute the soil and table

water (Impala Platinum Refineries waste streams, 2012). On the other hand, there is an abundant production of Fly Ash in South Africa. The latter is produced from the coal firing for power generation, which is listed as the main source of electricity production in South Africa. The main South African electricity producer generate approximately 36 million tons of Fly Ash per year (Eskom, 2011) while roughly 2 million tons of Fly Ash per annum is sold for reuse. Moreover, the remaining waste is dumped on a landfill adjacent to the power stations.

Clays are vital industrial raw materials. They are utilised in the fields of ceramics, paper, paint, petroleum industry, catalysis, ion exchange and clay materials are strong candidate as absorbents. (Preeti and Singh, 2007, Mortland et al, 1986, Burch and Warburton, 1987). This is largely because of their wide-ranging properties such as high resistance to atmospheric conditions, geochemical purity, and easy access to their deposits near the earth's surface and low price (Konta, 1995). Clays are widely used in the manufacturing of many traditional ceramic products such as bricks, porcelain, sanitary wares, floor and roofing tiles and in various industrial applications (Temimi et al, 1998; Sutcu et al, 2015; Oti et al, 2009; Oti and Kinuthia, 2012). Structural characterisation analysis allows for the identification of material based on its structural features. Almost all engineering materials exhibit structural features that can be identified using powder optical microscope.(Brandon and Kaplan, 2008). Furthermore, the characterisation and identification of minerals is fundamental in the development and operation of mining and minerals processing systems (Olubambi et al, 2008).

This paper focuses on the characterization of Jarosite, Fly Ash and Clay for the possible admixture to be used as construction materials. It is anticipated that the characterizations will provide more information on the quality of the hazardous sample such as Jarosite to further conduct investigations on the stabilization of hazardous elements to reduce their impact in the environment.

2. Materials and Experimental Methods

2.1. Materials and Mixtures

The Jarosite, Clay (plastic clay) and Fly ash samples were collected from Impala Base Metal Refinery, Vereeniging Refractories and Kelvin Power Station in South Africa respectively.

The moisture content of the collected samples was 15.63%, 0.82% and 0% for Jarosite, Fly Ash and Clay respectively. The physical mixtures were prepared by mixing preweighed amount of Jarosite and Clay in a mortar at a mass ratio of 1:1, 2:1 and 3:1, with a higher mass of Jarosite. 0, 5, 10, 15 and 20 % of Fly ash was added to the mixture and the samples were characterised.

2.2 Experimental Procedure

X-Ray Fluorescence analysis was performed on the raw and product samples to obtain their chemical compositions. The samples were oven dried overnight at around 105^0C. 10 grams of dried sample was used to make the pallets and samples were dried in an oven for 30 minutes at 50^oC. The XRF analyses were performed using a Rigaku ZSX Primus II, X-ray Fluorescence spectrometer (XRF).

X-Ray Diffraction (XRD) analysis was conducted to find the mineral phases present in the samples using a Rigaku, Ultima IV X-Ray diffractometer with monochromatic Cu Kα radiation at 40 kV, 30 mA. A Diffractogram was collected over a range of 2 theta between 3 and 90^o with a step size of 0.01, speed 1.

The surface morphology and chemical content of the granite sample was analysed using Scanning Electron Microscopy combined with Energy Dispersive X-ray spectrometer (SEM/EDS) respectively. A TESCAN (SEM) equipped with Oxford instrument X-Max (EDS), was used. Samples were crushed, mounted on a stud and carbons coated and irradiated with a beam of electrons at 20 Kv. Secondary Electron (SE) micrographs were produced and chemical analysis was carried out. Furthermore, A Micromeritics Accupyc1340 gas pycnometer and a Malvern Mastersizer 2000 particle size analyzer were used to measure the density and particle size distribution of the samples respectively.

3. Results and Discussion

The chemical compositions of the raw samples as obtained from the XRF analysis are shown in Table.1. It was concluded that the Fly ash analysed was in class F because it contains less than 20% of CaO. It was noticed that a large amount of Fe was found in the Jarosite sample (42%) compared to Clay (2.26%) and Fly ash (3.04%). Arsenic (As) and Lead (Pb) were also present in the Jarosite sample which shows the hazardous nature of the Jarosite and the importance of its stabilization to reduce its negative effect in the environment.

Table.1. Chemical compositions of the raw samples

	Raw materials		
	Jarosite	Clay	Fly ash
Elements	**% mass**		
Na	0.27	0.09	0.32
Mg	-	0.15	0.33
Al	1.74	20.01	18.42
Si	5.61	24.4	22.44
P	0.02	0.18	0.24
S	7.29	0.31	0.47
Cl	0.01	0.02	0.01
K	0.41	0.86	1
Ca	0.06	0.7	3.47
Ti	0.02	1.55	1.5
Cr	0.18	0.03	0.05
Mn	-	0.01	0.06
Fe	41.26	2.26	3.04
Co	0.04	-	-
Ni	3.69	0.01	0.02
Cu	0.01	0.01	0.01
As	0.59	-	-
Mo	0.01	-	-
Zn	-	0.01	0.01
Ga	-	0.01	0.01
Rb	-	0.01	0.01
Sr	-	0.12	0.22
Y	-	0.04	0.04
Zr	-	0.07	0.09
Ba	-	0.08	0.17
Pb	0.55	0.02	0.02
Th	-	0.01	0.01

It was noticed that by increasing the percentage of Fly ash in the ratios, the percentages of most the chemical elements increases as shown in Table.2. The percentage of Pb and As was decreasing by increasing the percentage of Fly ash.

Table.2. Chemical composition of the mixture (ratio 3:1) with different percentage of Fly ash

	Ratio3:1				
	0% ash	5% ash	10% ash	15%ash	20%ash
Elements			**% Mass**		
Na	0.25	0.3	0.32	0.34	0.36
Mg	0.08	0.11	0.14	0.17	0.22
Al	5.4	6.25	6.99	7.78	8.57
Si	8.46	9.49	10	10.66	11.31
P	0.04	0.05	0.06	0.07	0.07
S	6.65	6.29	6.05	5.73	5.49
Cl	0.01	0.02	-	0.01	0.01
K	0.46	0.51	0.52	0.54	0.57
Ca	0.13	0.3	0.46	0.59	0.74
Ti	0.22	0.3	0.33	0.4	0.44
Cr	0.16	0.14	0.14	0.14	0.13
Mn	0.01	0.03	0.05	0.06	0.09
Fe	33.29	31.48	30.08	28.47	26.65
Co	0.04	0.04	0.04	0.04	0.03
Ni	3.3	2.73	2.55	2.4	2.27
Cu	0.01	0.01	0.01	0.01	0.01
As	0.48	0.42	0.4	0.38	0.35
Nb	-	0	0	0	0
Rb	0	0	-	0	-
Sr	0.02	0.03	0.04	0.04	0.05
Y	-		-	-	-
Zr	0.03	0.02	0.02	0.02	0.02
Ba	0.08	0.08	0.05	0.08	0.11
Pb	0.41	0.4	0.37	0.35	0.34
Hg	-	0.01	-	-	0.01
V	-	0.01	0.01	-	-

The XRD results revealed that the main mineral phases in Jarosite are Coesite (SiO_2), Alacranite (AsS), Scrutinyite (PbO_2) and Jarosite (K ($Fe_3(SO_4)_2(OH)_6$)). This results also confirmed the presence of toxic elements such Pb, Ni and As. These toxic elements were present in a form of lead (IV) dilead (II) tetraoxide, Heazlewoodite and Alacranite.

The mineral phases in clay were Kaolinite ($Al_2Si_2O_5(OH)_4$), Anatase (TiO_2) and Quartz (SiO_2). This clay can be considered as a waste as it is low grade clay with weak binding properties (low amount of calcium), this was in agreement with the XRF results.

Fly ash major minerals phases were Mullite ($Al_{4.64}Si_{1.36}O_{9.68}$), Quartz ($SiO_2$) and Calcium oxide silicate chloride ($Ca_2O_2Si_3Cl_2$). Calcium oxide silicate chloride contained in fly ash was very minor (<1%) make it to be in class F a very weak binder as depicted in Fig.1.

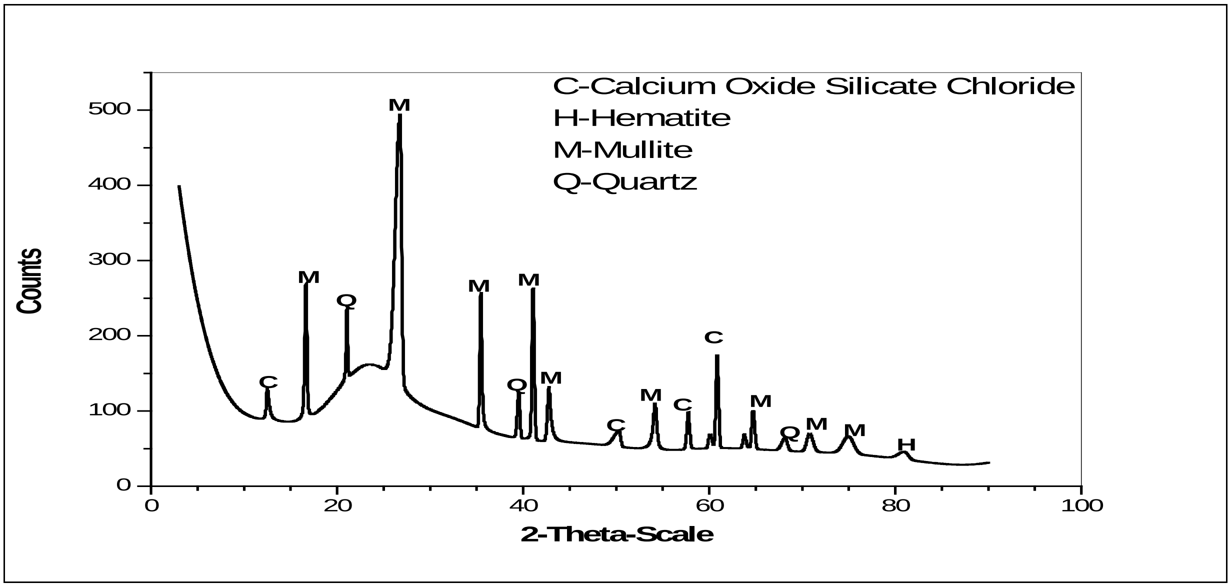

Fig.1. X-Ray diffractogram of the Fly ash showing the minerals identified.

The EDS results were in agreement with the XRF results that Jarosite contains great amount of iron, sulphur and silica oxides whereas clay and Fly ash main oxides are silica, aluminium oxide with iron and calcium respectively. It also confirmed the present of toxic elements that are in Jarosite such as lead, nickel and arsenic. From the microstructures it is seen that Jarosite and Clay are both irregular in shape and are not uniform in structure, whereas Fly ash microstructure revealed that it is regular and are cenosphere in nature and can also be spherical, it can also be seen that particles are not bonded (are loose) to one another which also prove that it contains no moisture due to its production process as a dust. Fig.2 shows the SEM micrograph of Jarosite, Clay and Fly ash whereas Fig.3 depicts an EDS spectrum from SEM micrograph of the Jarosite.

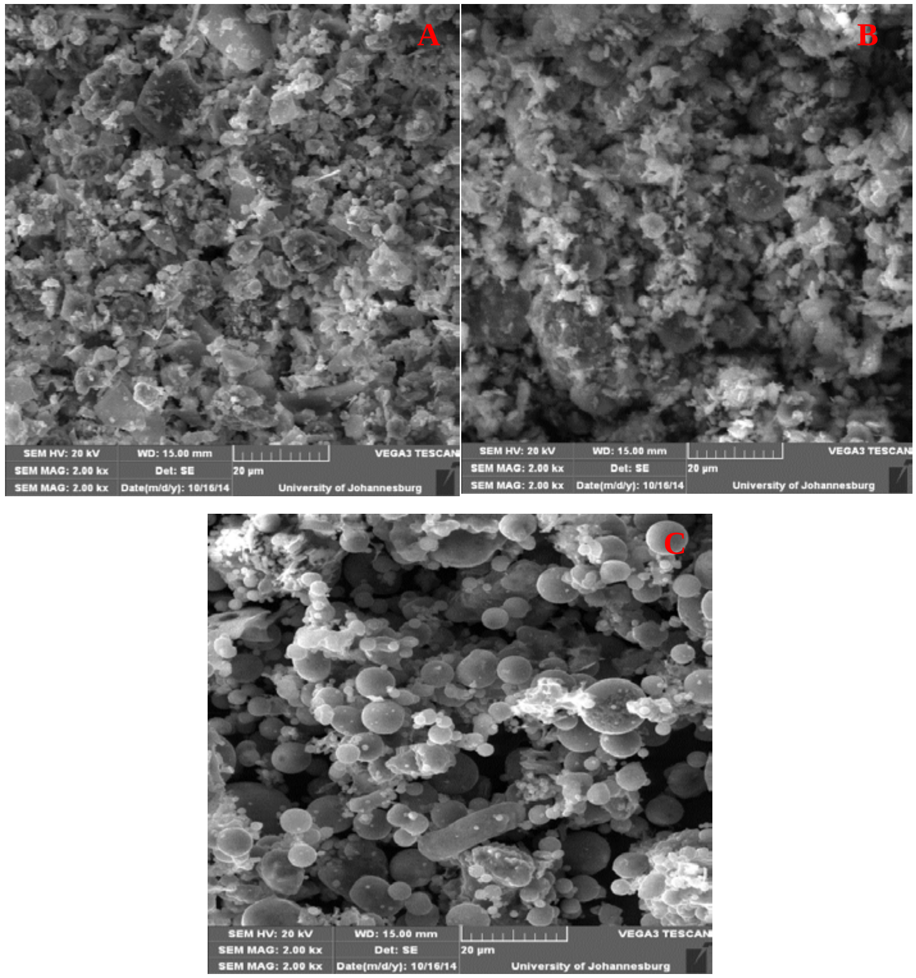

Fig.2. Showing Jarosite (A), Clay (B) and Fly ash (C) SEM microstructures

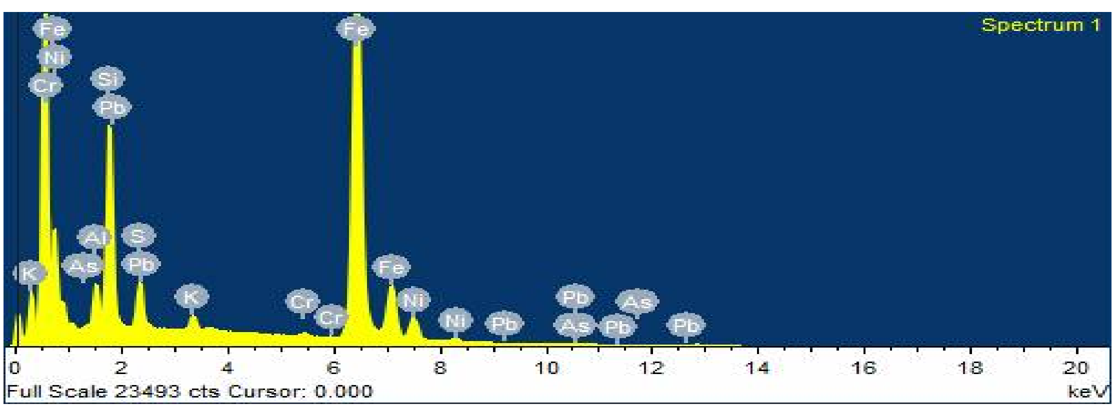

Fig.3. EDS spectrum of the Jarosite sample from SEM micrograph shown in Fig.2. (A)

The Jarosite had a minimum of 0.3 microns and a top size of 600 microns. A large portion of the sample was between 10 microns and 100 microns. Whereas, Fly ash particle size ranged from 0.4 microns to 800 microns. Furthermore, the clay sample particle size ranged from 0.4 microns to 200 microns. The Particle size Distributions of the Jarosite is shown in Fig.4.

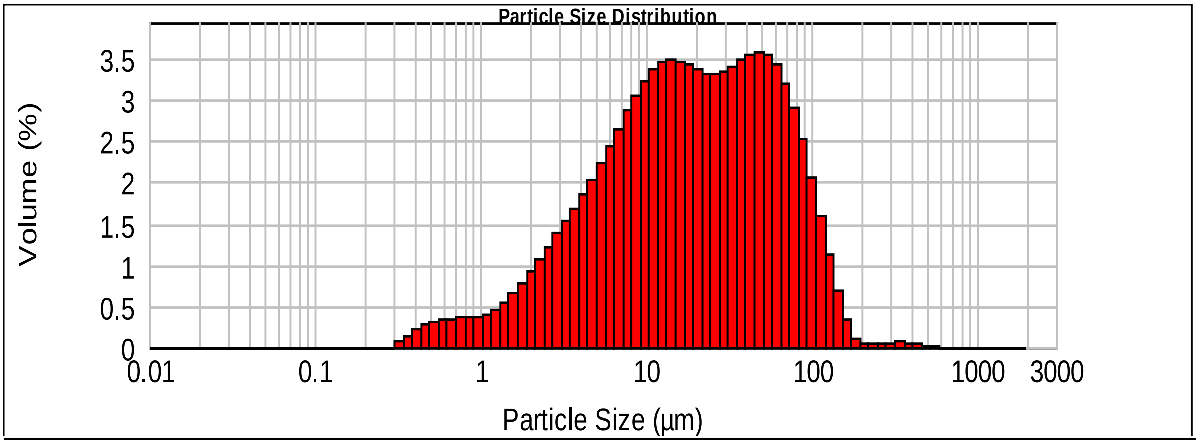

Fig.4. Jarosite particle size distribution

The densities of the raw samples were 3.13 g/cm^3, 2.67 g/cm^3 and 2.21 g/cm^3 respectively for Jarosite, Clay and Fly ash. Furthermore, the densities of the ratios and the one with an additional percentage of Fly ash were measured. Results depicted in Fig.5, revealed that there is an increase in density with the increase of the percentage of Jarosite. As it can be seen, raw Jarosite has the highest density and its influence can be clearly seen. On the other hand, the effect of Fly ash percentage addition in the mixture is seen. There is a decrease in density with the increase of Fly ash percentage addition; this can be attributed to its low density. Fig.6, 7 and 8 show the effect of Fly ash percentage addition on the densities of the mixtures.

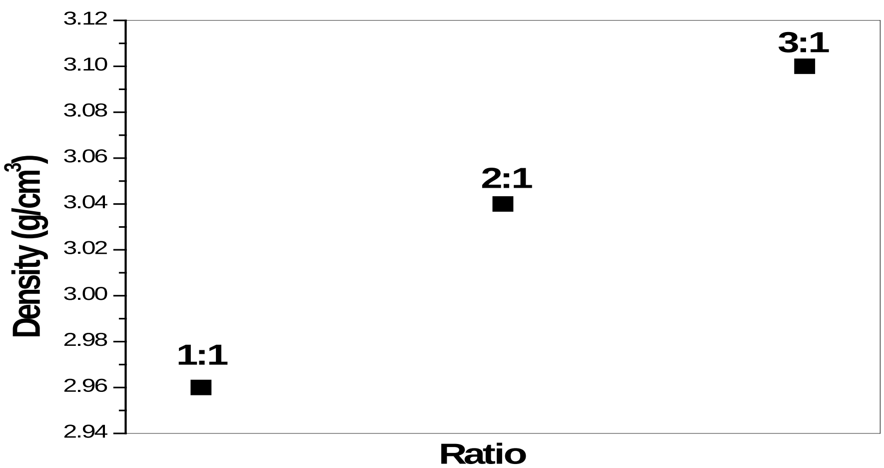

Fig.5. Density measurements of the different ratios

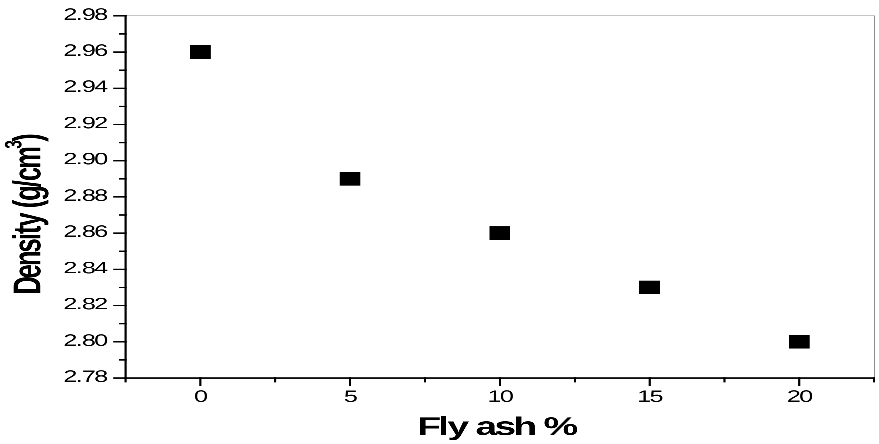

Fig.6. Showing the effect of Fly ash percentage addition on the ratio 1:1

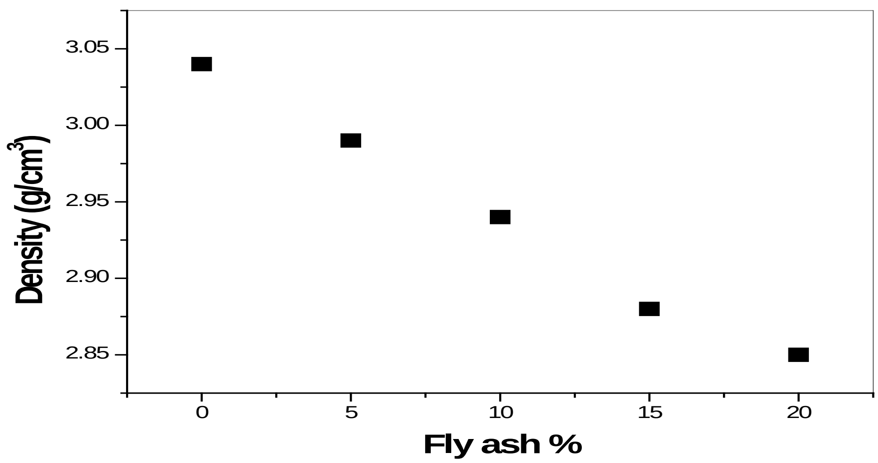

Fig.7. Showing the effect of Fly ash percentage addition on the ratio 2:1

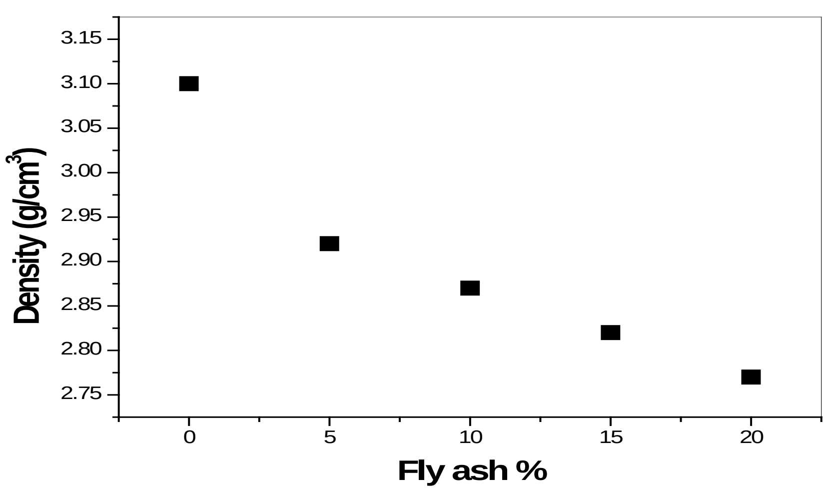

Fig.8. Showing the effect of Fly ash percentage addition on the ratio 3:1

4. Conclusion

The mineralogy and physical characterisation of Jarosite, clay and Fly ash from South Africa was conducted and it can be concluded that:

- The mineralogical composition of the Jarosite shows the presence of hazardous phases such as Alacranite (AsS) and Scrutinyite (PbO_2). The XRD also confirmed the presence of toxic elements such Pb, Ni and As. These toxic elements were present in a form of lead (IV) dilead (II) tetraoxide, Heazlewoodite and Alacranite.
- The XRF analysis concluded that the Fly ash analysed was in class F. A large amount of Fe was found in the Jarosite sample (42%) compared to Clay (2.26%) and Fly ash (3.04%). Arsenic (As) and Lead (Pb) were also present in the Jarosite.
- The Jarosite had a minimum of 0.3 microns and a top size of 600 microns. Whereas, Fly ash particle size ranged from 0.4 microns to 800 microns. Furthermore, the clay sample particle size ranged from 0.4 microns to 200 microns.
- The densities of the ratios increased with the increase of the Jarosite percentage in the mixture whereas a decrease was observed when the percentage of Fly ash was increase in the mixture of Jarosite and clay.

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