Journal of Materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 8, Page 2738-2746

http://www.jmaterenvironsci.com/

2'JP2E, 24-25 Oct. 2016, FP-Taza

Physicochemical characterization of an industrial waste: A case study of the pyrrhotite ash from south west of Morocco

M. Achik[1], A. Oulmekki[1], M. Ijjaali[1], H. Benmoussa[1, 2*], N. EL Moudden[2], S. EL Khattabi[3], R. EL Khattabi[4], F- Z. Ahjyyaj[5], G. Gonzalez Álvaro[6], F. Guitian Rivera[6].

[1]*Laboratory of Chemistry of Condensed Matter, Faculty of Science and Technology, Sidi Mohamed Ben Abdellah University, Fez, Morocco.*
[2]*Innovation Center, Sidi Mohamed Ben Abdellah University, Fez, Morocco.*
[3]*Laboratory of System Engineering and Applications, National School of Applied Sciences, Sidi Mohamed Ben Abdellah University, Fez, Morocco.*
[4]*Normal Higher School, Sidi Mohamed Ben Abdellah University, Fez, Morocco.*
[5]*Laboratory of Materials, Natural Substances, Environment and Modeling, Polydisciplinary Faculty of Taza, Sidi Mohamed Ben Abdellah University, Fez, Morocco.*
[6]*Galician Institute of Ceramics, University of Santiago de Compostela, Spain.*

Received 24 Jan 2017
Revised 16 Apr 2017
Accepted 18 Apr 2017

Keywords

- ✓ Pyrrhotite ash
- ✓ Minerals
- ✓ Industrial waste
- ✓ Hematite
- ✓ Thermal stability

hayat.benmoussa@usmba.ac.ma ,
Phone: (+212) 695598719

Abstract

This work concerned the physicochemical characterization of an industrial waste which is the pyrrhotite ash from south west of Morocco. A physical and hydrodynamic analyzes were carried out, namely loss on ignition, moisture content, pH, solubility, density and granulometry, as well as chemical, morphological and mineralogical analyzes by SEM, XRF, XRD,FTIR and TGA/DTA. The results show that the pyrrhotite ash is a non hygroscopic waste with a moisture content equal to 3.4%. This weak hygroscopic character is mainly attributed to the spherical morphology of the waste particles. The distribution of the particle size vary from less than 1 µm to more than 125 µm and more than three quarter of particles have size less than 20 µm. So, pyrrhotite ash could be useful to produce materials with high density for heat accumulation materials, construction materials…
Furthermore, the chemical composition reveals that the pyrrhotite ash is an iron rich waste with 64.9% of hematite Fe_2O_3. It contains 81.91% of Fe_2O_3 + SiO_2 + Al_2O_3 and 0.526% of CaO.
One the other hand, it is shown that pyrrhotite ash is a stable material at high temperatures until 1000°C and also at neutral pH.
At the end, all the cited results highlight the possibility of making the pyrrhotite ash very useful in various fields as building construction, heat accumulation materials, waste water treatment…

1. Introduction

Nowadays, the reuse of industrial solid wastes is a major challenge for scientists and industrialists. Recovery of these materials generates economic and environmental benefits. In fact, the reuse of industrial wastesallows developing resource-saving and environmentally friendly technologies, decreasing adverse impact on the environmentandthe landfilling of wastes in large disposal areas and reducing the cost of producing new products. Therefore, industrial wastes are widely studied in many areas of research. However, valorization of those wastes depends on their chemical composition, microstructure and physical and hydrodynamic properties. Industrial wastes containing iron oxide, silicon oxide, aluminum oxide - as major oxides at various content- such as fly ash (with major oxides:SiO_2, Al_2O_3, Fe_2O_3), pyrite ash (major oxide: Fe_2O_3), red mud (major oxides: Fe_2O_3, TiO_2, Al_2O_3, SiO_2), were studied and reused in various fields. There are many applications of these wastes. The following are some examples:

- The fly ash is mostly used inconcrete production, road basement material, waste stabilization/solidification, cement clinkers, and more recently geopolymer concrete[1, 2];
- The red mud is used to produce heat accumulator ceramic blocks[3, 4]. It is also used in plastic industry and that for production of pigments and bricks for the building industry, road construction and in agriculture [5];
- The pyrite ash is used to produce materials with high density for heat accumulation materials and road construction materials[6].

Pyrrhotite ash is an industrial solid waste, containing high concentration of hematite Fe_2O_3 and traces of other oxides[7, 8], which could be considered as belonging to the group of wastes cited above, but which didn't receive the attention of scientists in order to explore the areas of its application in industry. This waste was generated during the period between1964and1982 by the process of sulfuric acid manufacture from roastedpyrrhotite ore in south west of Morocco[9]. This process was proved to be unprofitable, and then it wasn't used anymore[8]. Thus, the unit of pyrrhotite roasting was replaced by another unit using the process of burning of the native sulfur. The pyrrhotite ash is currently stored in a large open space and any estimation of the stored quantity is available in literature. However, it is well known that during the above-mentioned period, 8 million tons of pyrrhotiteorewere extracted and used by the manufacture of sulfuric acid[10]; and that 429000 tons of sulfuric acid were produced annually[11]. These numbers expect that a huge quantity of pyrrhotite ash is stored. To the best of our knowledge only 150000 tons were recovered by Moroccan cement industries until 2011[7]. Definitely, there is an information gap regarding this waste in literature. In fact, anyscientificstudywaspublishedneither on the characterization of the pyrrhotite ash nor on the impact of this waste on the environment.So, the aimof the present research work is to study physico-chemical, mineralogical and morphological characteristics of the pyrrhotiteash,so that relevant and useful information on basic characteristics can be generated and may help carrying out further research: (i) to assess the impact of this waste on the environment and (ii) to suggest utilization of this waste as potential substitutes in some industries.

2. Materials and methods

2.1.Materials

Pyrrhotite ash samples were collected from an ash monofill located in south west of Morocco. This monofill was the sole disposal area of residue from roasting pyrrhotitefor the period between 1965 and 1982.

Three samples were retrieved from one slide slope in the north of the disposal area. The first one was collected on the surface and the two others from the depths of 0.5m and 1mrespectively.

Pyrrhotiteash is a solid waste powder consisting of fine and coarse grainswithoutodor at room temperature.Sampleswere collected andstored in plastic bottlesbefore analysis.

2.2.Physical and hydrodynamic analysis

- Determination of the average of moisture content consists on weighing specimens before and after drying at 120°C.The loss of weight makes possible to calculate the average of the moisturecontent;
- To measure the average of the loss on ignition, samples were crushed to fine particles with a small size in the micrometer range and then calcined at 1000°C for 6 hours;
  For determination of both moisture content and loss on ignition a WiseTherm type oven was used;
- The average of the Hydrogen potential of the pyrrhotite ash was measured on a water leach with a ratio of 10 L/kg of dry matter. The mixtureswere heated with refluxing at 100 °C for 16 hours. Then the mixtures were filtered and the pH of the filtrateswere measured [12].
- The solubility of the ash was tested in various acids of 2M concentration, using the reflux heating under magnetic stirring for 2 hours at 100°C.

The analyses cited above were performedin the Condensed Matter Chemistry Laboratory of University of Sidi Mohamed Ben Abdellah of Fez;

- Particle size distribution was conducted by the Sifting machine DIGITAL FI-FTL0150 & FI-FTL0200. To achieve this analysis, sample was grinded with a wooden roller. The median diameter of particleswasdetermined using the SediGraph 5100 instrument. This technique was used only for the fraction of ash with size smaller than 60µm and resulting from a previous granulometric separation realized by column of sieves.

- Density was measured by a Capillary cap pycnometer.

The latter analyseswere performed in the Galician Institute of Ceramics, University of Santiago de Compostela, Spain.

2.3. Chemical, mineralogical and morphological characteristics

- The mineralogical characteristics were determined by X-ray diffraction using Siemens D500 Diffractometer. The XRD patterns were performedin the range of 2θ between 2°and 60°with operating conditions of 40 kV and 50 mA;

- Thepresence of functional groups on the ash was investigated using Fourier transform infrared spectroscopy(JASCO 4000 Fourier Transform Spectrometer)in wavenumber range of4000-400 cm^{-1};

- The thermogravimetric analysis (TGA–DTA) has been performed with a TA Instruments balance model STA-1640. It allows obtaining simultaneous DTA and TGA diagrams under similar experimental conditions. Experiments were performed under an N_2 flow, from 298°K to 1073°K at a heating rate of 5°C/min;

These three analyses wereperformedin the Galician Institute of Ceramics, University of Santiago de Compostela, Spain.

- The morphological characteristics were determined for a calcined pellet of pyrrhotite ash at 900°C by Scanning Electron Microscopy (SEM).This was done using SEMHitch S-2500 microscope - operating with an acceleration voltage of 16kv - of the Innovation Center of Sidi Mohamed Ben Abdellah University in Fez, Morocco;

- Major and minor element analysis was conducted using X-ray fluorescence. The equipment used wastheWavelength dispersion spectrometer - Type Axiosof the National Center for Scientific and Technical Research in Rabat, Morocco.

3. Results and discussion

3.1. Physical and hydrodynamic analysis

The table1summarizes the average values of physical and hydrodynamicparameters

Table 1: Physical and hydrodynamic parameters of the pyrrhotite ash

Settings	H%	L.O.I %	pH	D
values	3.4	7.7	2.92	4.33

With: H: Moisture content;L.O.I: Loss OnIgnition at 1000°C; D: Density.

The results show that the pyrrhotite density isaround 4.33. The waste is non-hygroscopic with a low loss on ignitionthat could be mainly caused by the presence of elements as carbon and sulfur which are not burned during the process leading to this waste[13].
There were no discernable trends regarding the variation of physical and hydrodynamic parameters with depth. The results presented below are relative to the sampleretrieved from the depth of 0.5m.

3.1.1. Particle size distribution

The particle size distribution was determined for the dry ash using a vibrating sieve column. The results are shown in Figure 1. Particle size distribution of the pyrrhotite ash is continuous andcontains fractions of grains from a diameter 1 μmto125 μm. And it is known that the mixing of different fractions generally results in a compact material because the relatively small particles can be accommodated in the interstices between the larger ones. So, the material fills the volume more compactly[14].
A fraction of pyrrhotite ash which has a diameter less than 60 μm was analyzed by SediGraph 5100 instrument (this instrument analyses only samples that have particles less than100 μm). The results show that the mediandiameter($D_{0.5}$)is11 μm.

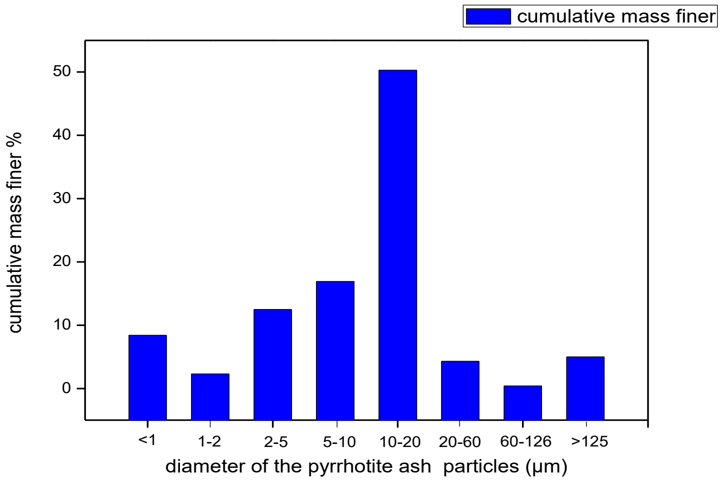

Figure 1: Histogram of grain size distribution of the pyrrhotite ash

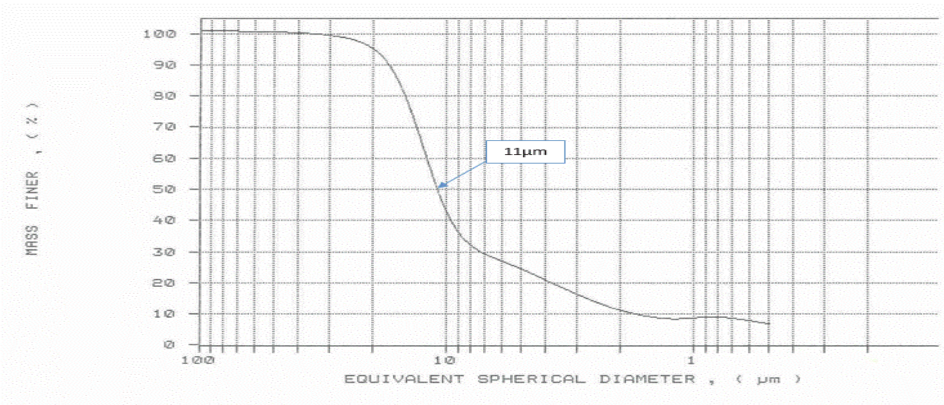

Figure 2: Cumulative particle size distribution of pyrrhotite ash(fraction less than 60 µm)

3.1.2. Solubility

The solubility rate of the pyrrhotite ash in variousacidshas been determined by means of the following relationship:

$$\frac{(\mathbf{wi}-\mathbf{wf})\ *\ \mathbf{100}}{\mathbf{wi}}$$

w_i: is the initial weight of the pyrrhotite ash
w_f : is the final weightof the pyrrhotite ash

The obtained results are given in Table 2.The ash is more soluble in the hydrochloric acid than the other acids.

Table 2: Solubilityrate of the pyrrhotite ash in various acids of 2M concentration

Acid	**HNO_3**	**H_2SO_4**	**H_3PO_4**	**HCl**
Solubility rate of the ash	40%	54%	60%	64%

The 100%solubilityratewasobtainedfor the concentration of 8M according to the following protocol:Mix 0.5 g of the ash with 100 ml of HCl(8M)and then make the mixture in a refluxing heater at 120°C for 22 hourswith a magnetic stirring model “C-MAG HS 7”.
This result is in accordance with the previous work[15]related to the study of the fly ash leachability under acidic conditions for the extraction of metal elements.It has been reported that when the fly ash -that is rich in aluminum

and iron oxides - contacts with hydrochloric acid, most of the metals such as Fe and Al can leach into the solution through the following reactions:

$$Fe_2O_3 + 6H^+ \rightarrow Fe^{+3} + 3H_2O$$
$$Fe_3O_4 + 8H^+ \rightarrow Fe^{+2} + 2Fe^{+3} + 4H_2O$$
$$Al_2O_3 + 6H^+ \rightarrow 2Al^{+3} + 3H_2O$$

3.1.3. Solubility rate of the pyrrhotite ash versus pH

0.5 g of ash was mixed with 100 ml of solvent (HCl for acid pH, NaOH for basic pH) at various concentrations. For the neutral pH, distilled water was used as solvent. Hydrochloric acid was chosen since thepyrrhotite ash had a high solubilization rate (64%) as stated in the table 2.

The mixtureswereheated at refluxfor 3 hours and then filtered. The collected solid is weighed after drying.

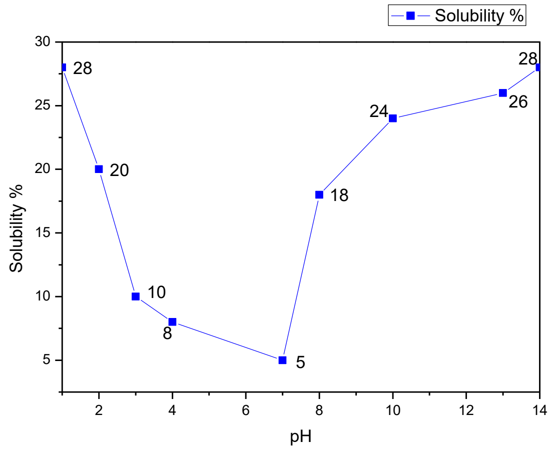

Figure3: Solubility rate vs the pH

It is noted that the solubility rate of the pyrrhotite ash increaseswith increasing of acidity or basicity of the solution.The lowest solubility rate of pyrrhotite ash is obtained at neutral pH.

3.2. Chemical, mineralogical and morphological analysis

3.2.1. Scanning electron microscopy (SEM)

The morphology of the ash as observed from SEM measurements is shown in Figure 4. The particle shape is reported to be spherical with some of the particlesseen to be tightly attached to each other, forming agglomerates.Thismorphological analysis highlightsalso the sinteringeffect between grains and confirms the variation in particle size of the spheres, as observed by particle size determination.

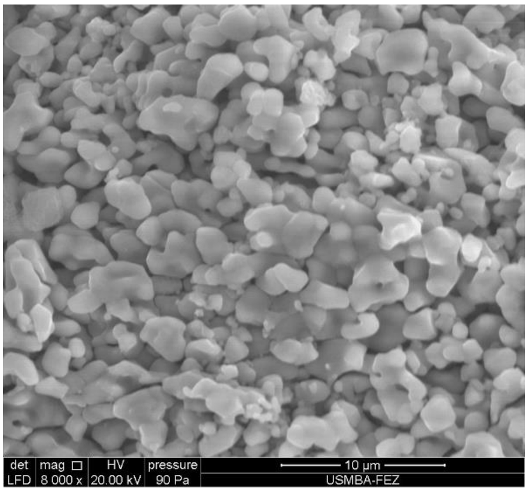

Figure 4:SEM micrograph of pyrrhotite ash

Figure 4 shows also thatthe spheres have a relatively smooth surface and it isobviousthatparticles having a spherical shape with a smooth surface don't retain water. Thiscouldconfer to the pyrrhotite ash anon-hygroscopic character as indicated above in the section 3.1.

A similar morphology was seen for the fly ash for which it has been reported in literaturethat the spherical shape ofits particles leads to a positive effect on the workability and cohesiveness when they areusedascementsreplacement material in concretes and mortars[16, 17].

3.2.2. X-Ray Fluorescence spectrometry (XRF)

Thechemical composition of the pyrrhotite ash provided by fluorescence X is given in Table 3. It is shown that iron oxide (hematite Fe_2O_3)andsilicon dioxide(quartz SiO_2) are the major constituents of the pyrrhotiteash with concentrations of 64.9% and 13% respectively.Minor proportions of Al_2O_3,SO_3, MgO, P_2O_5 and Cr_2O_3 are also present with total concentration of 15.63%. Traces of CaO, K_2O, Na_2O, MnO_2, NiO, TiO_2, CoO, ZnOare also present.

Table 3: Chemicalanalysisdataforpyrrhotiteash.

Oxides	Fe_2O_3	SiO_2	Al_2O_3	SO_3	MgO	P_2O_5	Cr_2O_3	Na_2O	NiO	CaO	MnO_2	K_2O	TiO_2	CoO	ZnO	MoO_3
Wt %	64.9	13	4.01	3.96	2.73	2.7	2.23	0.662	0.626	0.526	0.336	0.139	0.111	0.0764	0,0402	0,0274
Elements	**Fe**	**O**	**Si**	**Al**	**Mg**	**S**	**Cr**	**P**	**C**	**Ni**	**Na**	**Ca**	**Mn**	**K**	**Cl**	**Ti**
Wt %	45.4	37.2	6.1	2.12	1.65	1.59	1.52	1.18	0.917	0.492	0.491	0.376	0.212	0.115	0.111	0.0668

The obtained results confirm the acidity of pyrrhotite ash as the Ca / S ratio = 0.376 / 1.59 = 0.24 <2.5 [18].

Generally, the reuse of ash depends mainly on its chemical composition.It has been reported in literature[16, 19]that fly ash containingmore than70% of SiO_2 + Al_2O_3 + Fe_2O_3 with a low content of calcium exhibits pozzolanic properties but possesses little or no self hardening property. Thus, it is expected that pyrrhotite ash which contains 81.91% of Fe_2O_3+ SiO_2 + Al_2O_3 and a low percentage of calcium could exhibits a pozzolanic property and this explains the use of the pyrrhotite ash by some cement industries[20]. It is also noticed that Pyrrhotite ash contains a very high percentage of Fe_2O_3(64.9%) than the fly ash[2]which could improve mechanical properties of construction materials[21].

On the other hand, the XRF analysis reveals the presence of SO_3 with concentration of 3.96% (equivalent to 1.59% S) in the pyrrhotite ash. This indicates that, despite its iron rich composition, the pyrrhotite ash can't be reused in the metallurgical industry[22]. It is well known that sulfur is a weakening element as soon as its content exceeds 0.08%[23].

3.2.3. X-Ray Diffraction (XRD)

Figure 5 illustrates the X-ray diffraction pattern of the pyrrhotite ash.

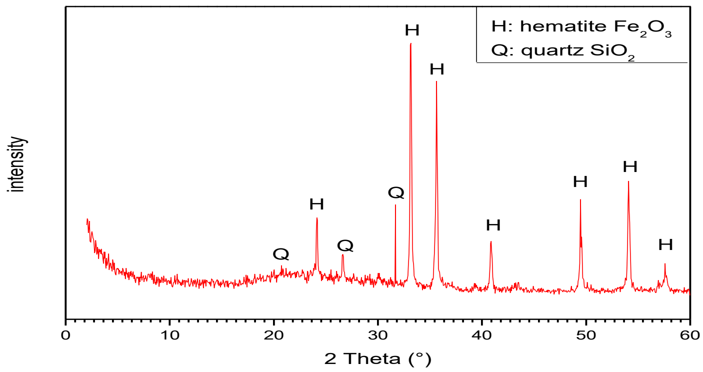

Figure 5: DiffractogramXof the pyrrhotite ash.

The X-ray diffraction diagram shows the presence of the following peaks:

2 theta = 24,3° ; 33,2° ; 35,6° ; 41° ; 49,5° ; 54° ; 57,5° characteristicpeaks of the hematite phase(Fe_2O_3) [24];

2 theta = 21°; 26,5°; 31,9°characteristicpeaksof the quartz (SiO_2)phase[25].
The main diffraction peaks are assigned to hematite (Fe_2O_3) and quartz phases(SiO_2).
Aluminum mineralogical phase is not observed in the diffractogram as the content of $Al_2O_3$is approximately 4% as shown by X-ray fluorescence (Table 3). Thus, hematite is denoted as the maincrystalline phase along with minor contentofquartzconfirming the results obtained by X-ray fluorescence.

3.2.4. Fourier Transform Infrared Spectrometry (FTIR)
The infrared absorption spectrum obtained for the pyrrhotiteash is illustrated in Figure 6.

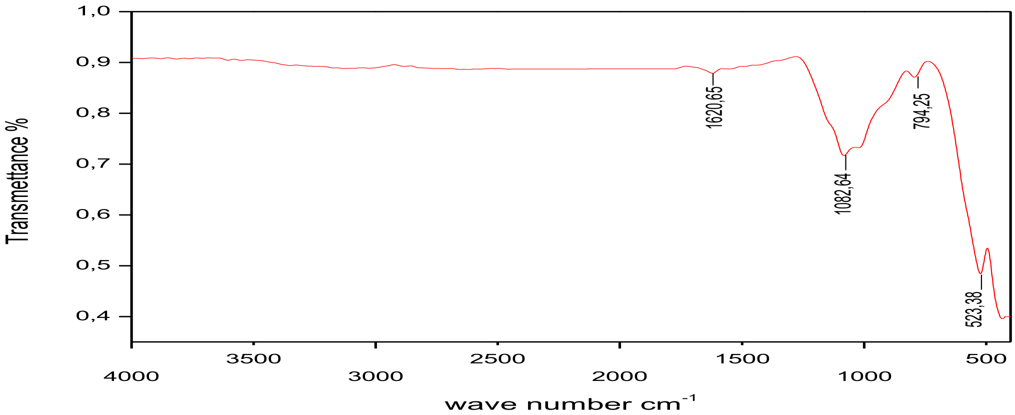

Figure 6: Fourier Transform Infrared spectrum of the pyrrhotite ash

The main absorption bands found on the spectrum are given in Table 4. Bands characterizing oxides of metals lies between 400-1500 cm^{-1}[26].It is noted a very small band related to traces of water moleculesthat confirms the character non hygroscopic of the ash as stated above.

Table4: Main absorption bands of pyrrhotite ash

Frequency in cm^{-1}	Attribution
1620,65	Deformation of water molecules OH-H
1082,64	Bond elongation $^{\nu}$Si-O
794,25	Link elongation vibration$^{\nu}$Si-O
523,38	Bond elongation $^{\nu}$Fe-O

The results obtained in the analysis of infrared spectrometry are compatible with those presented by X-ray diffraction and X-ray fluorescence.

3.2.5 Thermogravimetric and Differential thermal analysis (TGA/DTA)
The TGA / DTA curves of pyrrhotite ash are shown in Figure 7.

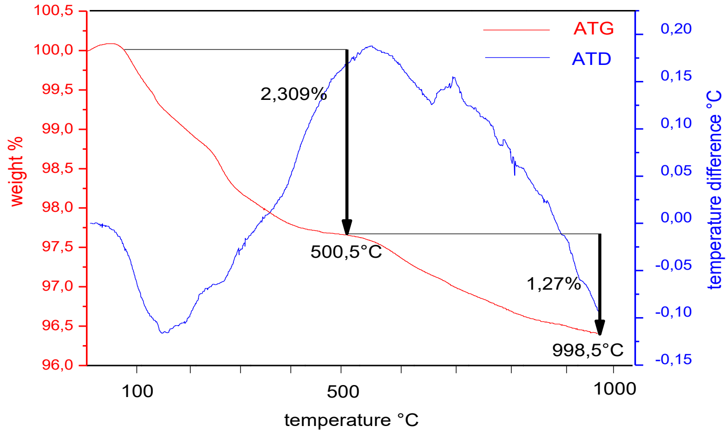

Figure 7:TGA/DTA analysis of the pyrrhotite ash

The TGA spectrum shows a weight loss of 3%. This is associated initially with water loss. The broad band between 300–1000 ºC is related to the elimination of SO_3/SO_2.There is no thermic effect in the analysis. The pyrrhotite ash is mainly composed by hematite Fe_2O_3, small amount of quartz $SiO_2$and traces of other oxides. The hematite Fe_2O_3 is inert to the thermic analysis and no thermic effects are expected in the range of temperatures less than 1000°C.

3.3. Discussion

Pyrrhotite ash is a solid wastecontaininga very high percentage of hematite (64.9%of Fe_2O_3), small amount of quartz (16% of SiO_2)and traces of other oxides.It contains 81.91% ofFe_2O_3+ SiO_2 + Al_2O_3 and 0.526% of CaO. Thischemical composition could confer to the pyrrhotiteashaninteresting pozzolanicpropertywhichis appreciated in the field of construction materials. Further, pyrrhotite ash physical properties, especially the size and the spherical shape of particles could play an important role on the reuse of this waste.As shown in the case of fly ash, the spherical shape increasesthe workability and consistency of mortars and concretes [27].

Moreover, the small size of the pyrrhotite ash particles- almost three quarters of particleshave size less than 20µm- will allow the reuse of the waste without providing much effort for grinding. Also, it could allow the reuse of the waste to produce materials with high density for application in the building industry, road construction and heat accumulation materials, as it was shown for the pyrite ash and red mud which are also hematite rich wastes[3, 4, 6].

Furthermore, the stability of the pyrrhotite ash at neutral pH suggests studying the possibility of its use in the treatment of wastewater. On the other hand, its thermal stability will make possible to broaden the field of pyrrhotite ash application to high temperatures.

As it is stated above, the presence of sulfur (3.96% of SO_3)doesn't allow the reuse of the pyrrhotite ash in metallurgical industry, but it could be a good reason to carry out research works in order to reuse it in agriculture. Moreover, the pyrrhotite ash is a rich hematite waste that could present interesting magnetic properties. Also, it could be recovered in fields based on iron compounds (iron oxide, iron salts, iron complexes, etc.), since such compounds have a wide spectrum of use in the fields of dyes, waste water treatment, agro-food industry, etc.

Finally, the pyrrhotite ash is an acid waste and it is known from literature review that the maximumamount of heavy metals gets released under acidic environment [28]. And therefore, the study of the leaching of this waste is crucial for predicting environmental risks.

Conclusion

In the presentwork, the characterization of the pyrrhotiteashwhichis an industrialwaste from south west of Morocco has been investigated. The obtained results reveal that the pyrrhotiteash is an iron rich waste that is acid, non-hygroscopic and completely soluble in hydrochloric acid (8M). Moreover, this waste is stable at neutral pH and at High temperature. Its chemical composition and morphological and physical properties are promising in terms of the reuse of this waste- as whole or partialreplacement-in constructionmaterials,highways construction, production of dense materials for heat accumulation, agriculture, waste water treatment…

In order to better exploit this waste, it is suitable to carry out some research works on the mechanical, thermal, magnetic and electrical properties of the pyrrhotite ash.

Acknowledgments-The authors would like to thank the technical staff of Galician Institute of Ceramics of University of Santiago de Compostela in Spain for their support which is greatly appreciated.

References

1. El MoudniS., AlamiE., and MonkadeM.,"Valorization of the fly ash from jorf lasfar thermal power station in cement : mechanical and environmental study valorisation des cendres volantes de la centrale thermique de jorf lasfar dans les ciments : etude mecanique et environnementale," vol. 51, no. January, pp. 38–45, (2010).
2. Hemalatha T. and RamaswamyA.,*Journal of Cleaner Production*, 147 (2017) 546–559.
3. Rodriguez G. A. P., "Obtencion de Ladrillos Acumuladores de Calor a partir de Lodos Rojos." Instituto de Ceramica de Galicia, Santiago Spain, p. 338(1999).
4. Rivera G., "Procediminiento para la obtencion de bloques ceramicos acumuladores de calor a partir de barros rojos del Proceso Bayer," ES 2 099 033(1997).
5. RodriguezG.P., Rivera F. G., and PendasS. D. A.,*Ceramica y Vidrio*, Santiago Spain, pp. 220–226(1999).
6. RiveraG., MesaF. G., TouronC.-P.,*"Procedimiento de obtencion de materiales ceramicos de alta densidad a*

partir de cenizas de piritas," ES 2 126 478(1999).
7. RicciM. , TaziS.,LaajajR., and SandöL., "OCP rapport annuel 2011 créer de la valeur, s'engager socialement.," *Logos Conseil, Casablanca*, vol. D, pp. 1–14(2011).
8 OualalouF., "La politique phosphatière marocaine et les tentatives d adaptation aux variations," p. 70 (2012).
9. NaoumiS.*"Matériaux de construction: Un projet de centre de broyage en Guinée Conakry digné Ciments du Maroc."*(2015).
10.EssaifiA., "L' ancienne Mine de pyrrhotite de Kettara (Jebilet centrales).," *researchgate*, no. March, pp. 205–209(2017).
11.Commission economique pour L'Afrique, "Etude par pays des ressources en matières premières destin"es à l'industrie des engrais en Afrique," in *deuxième confèrence régionale sur la mise en valeur et l'utilisation des ressources minérales en Afrique*, (1985) p. 30.
12.OlivierP., "Apports méthodologiques pour la modélisation du comportement à la lixiviation de résidus minéraux . Application aux solidifiats de boues d ' hydroxydes métalliques." (2008).
13.Frolova I. V., Tikhonov V. V., Poltoranina A. P., CherkashinaK. Y., and Shuangcheng F., *Procedia Chemistry*, 15 (2015) 272–276.
14.Malakhova A. A., MosinaV. M., GorlushkoD. A., NalesnikO. I., and Usoltseva N. V., *Procedia Chemistry*,15 (2015) 27–32.
15. Hosseini S. M. , Masomi M., Hosseini M., Javadian H.,RuizM., and SastreA. M.,*Process Safety and Environmental Protection*, 107 (6) (2017) 153–167.
16. SowM., HotJ., Tribout C., and Cyr M.,*Fuel*., 162 (2015) 224–233.
17. Sua-iamG., MakulN.,*Construction and Building Materials*, 95 (2015) 736–747.
18. SioD. "Cendres volantes," *observation Français des Resources des les InFrastructures*,1996 (2013) 1–23.
19.HamzaouiR., BouchenafaO. , GuessasmaS., LeklouN.,Bouaziz A., *Materials & Design*, 90 (2016) 29–37.
20.Quénée B. and SouchuP., " Les cendres volantes," *LERM INFOS N°26*, (2014).
21.Gerasimova E., *Procedia Engineering*, 150 (2016) 1553–1557.
22.Oliveira M. L. S.,*Science of The Total Environment*, 430 (2012) 34–47.
23. ChezeauN.,"De Réaumur à la Première Guerre Mondiale: les étapes de la maîtrise de l'acier, l'essor des aciers spéciaux,' *Comptes Rendus Chimie*, 15 (2012), no. 7, pp. 585–594, 2012.
24.Rihab L., "Nouveau procede d'élaboration de micro Et nanoparticules d'oxyde de fer en voie seche: caracterisation, étude du procede et proposition d'un mecanisme reactionnel," (2016).
25.NovaC. L.," Otimization of rational mineralogical analysis of ceramics), 51 (2005) 387–391.
26.JeddiS., OuassiniA., El OuahhabyM., and MghafriH., *Journal of Materials and Environmental Science*, 7(2) (2016) 488–496.
27. BaezaF., PayáJ., GalaoO., Saval J.M., and Garcés P., *Construction and Building Materials*, 66 (2014) 645–653.
28. Tiwari M. K., Bajpai S.,DewanganU. K, and Tamrakar R. K.,*Journal of Radiation Research and Applied Sciences*, 8(4) (2015) 523–537.

(2017) ; http://www.jmaterenvironsci.com