Environmental study and valorization of an ashy waste: case of pyrrhotite ash

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Abstract. Pyrrhotite ash is an industrial waste which is currently stored in large quantities in a large area in southwest of Morocco. The literature review revealed that this waste has been used by some cement industries and has not been the subject of any environmental study or valuation in another area. This work focuses on the environmental study of pyrrhotite ash. This study consists of a dynamic test with renewing lixiviate more particularly the leaching tank test. The protocol used is extracted from the Dutch standard NEN 7345 with modification of the volume of water used and the number of extraction. Quantitative analysis by ICP has shown that pyrrhotite ash releases heavy metals in aqueous medium. However, the concentration of these is very low compared to the limits estimated by the Dutch standard adapted to the Moroccan hydrological context (MBMD), this result encouraged us to find a way to valorise this waste and to make it a raw material for the manufacture of terracotta bricks made of clay.

1. Introduction
Nowadays, scientific research focuses more on the optimization of industrial processes, whether to increase profitability or minimize the rejection of these processes. The so-called minimization of industrial discharges says environmental protection, the latter becomes the main issue of the world. In fact, not only the minimization but also the reuse of industrial waste can develop environmentally friendly technologies, reduce the negative impact on the environment and the landfill of waste in large areas of storage and disposal. Reduce the cost of producing new products. As a result, industrial waste is widely studied in many areas of research.

In our research project we chose to study the waste of pyrrhotite ash, which is an industrial waste solid containing a high concentration of $\text{Fe}_2\text{O}_3$ hematite and traces of other oxides \cite{1}\cite{2}, this waste has not attracted the attention of scientists in order to explore the areas of its application in the industry. This waste was generated between 1964 and 1982 by the process of manufacturing sulfuric acid from grilled pyrrhotite ore in southwestern Morocco \cite{3}. This process proved unprofitable and was no longer used \cite{2}. Thus, the combustion unit of pyrrhotite has been replaced by another unit using the process of burning native sulfur as the price of the latter has decreased worldwide. Pyrrhotite ash is currently stored in a large open space. However, it is well known that during the above-mentioned period, 8 million tons of pyrrhotite ore were mined and used for the production of sulfuric acid \cite{4}; and that 429,000 tons of sulfuric acid were produced each year \cite{5}. These numbers expect a large amount of pyrrhotite ash to be stored. To our knowledge, only 150,000 tons were recovered by Moroccan cement industries until 2011 \cite{1}. 

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Therefore the recovery of these waste requires an environmental study to identify the chemical stability of this waste.

In a previous work[6], we chose to make a characteristic study for pyrrhotite ash, especially since the bibliographic study did not reveal any similar study.

As a result, we found many features of pyrrhotite ash that allowed its reuse in the construction sector. Among these properties we quote:

- The spherical shape of particles with a smooth surface that facilitates the incorporation of ash into the matrix of bricks and which can also affect the physical behavior of the bricks thus manufactured.
- The presence of the fluxing elements, namely the oxides of K₂O + Na₂O + CaO + MgO with a percentage of 4.057% which allows the use of this waste in the manufacture of fired bricks.[7]

The results found were satisfactory and according to the literature it has been found that pyrrhotite ash can serve as a raw material used to improve the properties of materials intended for construction and to minimize the rate of use of clay. For this reason the direction of our work directed towards the study of the chemical stability of this waste.

In this work, we have chosen to use leaching test [8] to study the environmental behavior of pyrrhotite ash, which is an industrial waste produced during the production of sulfuric acid from the pyrrhotite ore at the Kettara mine. This process was used since 1964 until 1982.

1982 is the year when the Kettara mine closed and so the process leading to the pyrrhotite ash was stopped.

2. Method and materials

2.1. Characterization of pyrrhotite ash:

To better understand the waste with which we will work and for which we wish to apply an appropriate valuation, it was necessary to disclose at least its chemico-physical characteristics, and since the literature has not presented any work of study for this waste, we had to first make a physical and chemical characterization for the pyrrhotite ash. This study was published [6] and the results were summarized table 1.

2.2. Environmental study

Table 1. Summary of the characteristic study of pyrrhotite ash.

| Parameter analysed | Results |
|--------------------|---------|
| Physical           |         |
| Particle size      | Particle size distribution of the pyrrhotite ash is continuous and contains fractions of grains from a diameter 1 µm to 125 µm. the median diameter (D0.5) is 11 µm; 4.33 g.cm⁻³; |
| Grain density      |         |
| Chemical           |         |
| DRX                | Characteristic peaks of the hematite and the quartz phases; |
| DFX                | Major oxides are: Fe₂O₃ (64.9%); SiO₂ (13.0%); Al₂O₃ (4.01%); |
| Mineralogical      |         |
| IR-Fourrier        | Bands characterizing oxides of metals (νSi-O ; νFe-O ); |
| SEM                | The particles have a spherical shape with a smooth surface; |
| Thermal            |         |
| ATD/ATG            | There is no thermic effect in the analysis; |
The raw material used for this work is pyrrhotite ash. Which is currently stored in large quantities in a large area in the Middle West of Morocco; figure 1.
The methods adopted to approach the environmental study are:

- Leaching tank test which is taken from the Dutch standard NEN 7345 [9] [10] [11];
- Tank test to identify wastes categories according to 7345:94 [12] [13];
- Quantitative analysis by ICP-AES for the extract.

Figure 1. Stock of pyrrhotite ash.

2.2.1. The protocol of the leaching test NEN-7345:[14]
First, the specimen to be tested must be aged 28 days from the total weight stabilization and shrinkage;
Secondly, the extraction fluid used is distilled water at pH = 6.7 with a volume ratio of the liquid/volume of the solid = 3;
The leachate samples are taken as follows:
The leachate was removed and replaced every 3 days for the first 21 days, then every 7 days for the next 14 days and finally every 14 days to complete 91 days from the start of the test, so in total we will have 13 catches; the same volume of leach was used for each renewal.
After each sample collection, the leachate was filtered at 0.45 µm, then the pH is measured, then the solution is acidified to pH [0.9-1.1] and analyzed by ICP (each sample is analyzed at least 3 times) ; in our case, we used concentrated nitric acid HNO3.
The results of the leachate quantitative analysis as a function of the day of contact between the pyrrhotite ash briquette and the distilled water are presented in the followings figures:

2.2.2. NEN-7345:94 (tank test)
This test allow us to identify the waste category, for that the measure leaching per fraction was calculated by the following formulas:

\[ E_i = \frac{C_i \cdot V}{f \cdot A} \left( \frac{mg}{m^2} \right) \] (1)

Where \( C_i \) is the concentration of the component in fraction i (µm/l),
\( V \) is the volume of the eluate in l;
\( A \) is the surface area of the test piece in m2;
\( f \) is a conversion factor: 1000 (µg/mg).
The materials are classified figure 2, as a function of cumulative leaching value which is calculated by equation 2 for each component:

\[ \varepsilon_i = \sum_{i=1}^{n} E_i \text{ for } n = 1 \text{ to } N \]  

(2)

Where N is the number of periods (N=13 for this test).

**Figure 2.** Classification of wastes according to the cumulative results (Σmg/m²).

3. Results and discussions

a)  

**Figure 3.** Concentration of heavy metals in the leachate of pyrrhotite ash (g / l).

(a) Cd content; (b) Cr content; (c) Pb content; (d) Zn content.
Figure 4. pH of leachate versus time of water-pyrrhotite ash contact.

The result obtained by the ICP quantitative analysis shows that the pyrrhotite ash releases heavy metals in an aqueous medium (figure 3), but the concentrations of the latter thus obtained remain very low compared to the limits estimated by the Dutch standard adapted to the Moroccan hydrological context (MBMD).[9] These results are consistent with the variation of the pH of the medium, which remains neutral to basic (figure 4) varies between [6.76 –7.98], this medium which tends towards the basicity does not favor the release of certain elements like the chromium by example that is released in acidic pH.

Table 2. NEN 7345:94 Cumulative result (Σ mg/m²).

|       | U1 (mg/m²) | U2 (mg/m²) | PA      |
|-------|------------|------------|---------|
| Pb    | 100        | 800        | 96,105  |
| Cd    | 1          | 7.5        | 0,929   |
| Cr    | 150        | 950        | 46,480  |
| Zn    | 200        | 1500       | 45,044  |

After studying the concentration of heavy metals (Pb, Cd, Cr, and Zn), the value $\xi_i$ was calculated as shown in the part 2.2.2, the results are shown in Table 2. It is clear that pyrrhotite ash can be classified in the category of waste that can be reused in materials intended for construction. Since the cumulative results of the heavy metals studied are all lower than the limit U1.[13][12][15].

4. Conclusion

To conclude, it is very clear that pyrrhotite ash does not have a negative effect on the environment, even if it produces heavy metals, but with concentrations that remain within the limits required by NEN 7345:94.

This result led us to reuse this waste and to value it in the manufacture of terracotta bricks, especially since the main constituents of AP are Fe$_2$O$_3$ and SiO$_2$ with concentrations of 64.9% and 13.0%, respectively of Al$_2$O$_3$, SO$_3$, MgO, P$_2$O$_5$ and Cr$_2$O$_3$ are with a total concentration of 15.63%, and traces of CaO, K$_2$O, Na$_2$O, MnO$_2$, NiO, TiO$_2$, CoO, ZnO are also presented (Table 1). The ratio Ca / S = 0.24 is less than 2.5 [16] which confirms the acidity of the pyrrhotite ashes as indicated in our previous work, the pH of the CP is 2.3 [6]. The fluxing elements, to know more the oxides of K$_2$O + Na$_2$O + CaO +
MgO are present in CP with a percentage of 4.057% which makes it possible to transform them into manufacture of cooked bricks. [7]

And since the pyrrhotite ash will substitute the rate of the clay material used. It will reduce the non-renewable natural resources, protect the environment and develop the economic sector.

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