

# Use of Geopolymers in the Treatment of Water Contaminated by Industrial Waste

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**Abstract.** The present research aimed to study the use of geopolymers in the removal of heavy metals in water contaminated by an industrial waste. The geopolymer was synthesized and characterized beforehand in the laboratory while the industrial waste is the so-called zinc ferrite that comes from a zinc processing industry in southern Italy. It is known that this waste contains within it a variety of elements that over time can be released if in contact with water. The study was carried out preparing different aqueous systems containing predetermined quantities of zinc ferrite and geopolymer. The systems were stirred for different reaction times and at room temperature. Subsequently, after the established time the systems were filtered and the resulting solution was analyzed by a mass spectrometer (ICP-MS). The variation in the concentration of various elements (such as Fe, Zn, Pb, Mn, Ca, Mg, Na and K) was followed as a function of contact times. The obtained data allowed to evaluate the effectiveness of geopolymers in the removal of metals released by zinc ferrite in water. In particular, the geopolymers, in the systems studied, have shown particular propensity in the abatement of iron and zinc which has reached 100%, followed by an abatement of about 95% for Mn and Pb after a 1.5-hour contact time.

## 1. Introduction

Many researchers are oriented to study industrial processes that are as environmentally sustainable as possible through the use of natural raw materials, the reduction of by-products or their reuse for the preparation of new materials that respect the environment [1-14]. The industrial by-products that are of particular concern are those waste containing heavy elements. This type of slag includes that from the zinc extraction process from the blende, the so-called zinc ferrite [15, 16]. Some recent studies report the removal of some elements released from this slag in water through the use of microporous materials [17]. The titanosilicates belonging to the Englarth Titanium Silicate (ETS) family characterized by a porous structure and properties such as ion exchange, catalysis, molecular sieving, photocatalysis [18-20], have been shown to be advantageously used for the removal of heavy metals in water contaminated with zinc ferrite [21].

In this research the action of geopolymers in the removal of some elements released by zinc ferrite in water was studied. Geopolymers are inorganic materials with a chemical composition similar to that of zeolites, but unlike these, they have an amorphous structure. The prefix "geo" indicates that the present



material is characterized by a mineralogical structure very similar to natural rocks, thus exhibiting similar properties, such as hardness, chemical stability and longevity. The term geopolymer aims to generally identify an amorphous or semi-crystalline alkaline-silicate alumino material, obtained by condensation polymerization, called geopolymerization or geosynthesis, or the reaction between an alumino-silicate powder with an aqueous solution of alkaline hydroxides or silicates [22-25].

## 2. Materials and methods

The zinc ferrite used appears as a material of intense brown color, grainy and characterized by a certain humidity since it comes from open-air storage [17]. Before testing, the latter was dried for two hours in an oven at 100 °C to eliminate the moisture present in it. Subsequently the dry material was finely ground in a mortar mill to ensure adequate homogeneity. The geopolymers that have been used to study their potential use in the removal of metals released from ferrite in water have been previously synthesized in the laboratory. The latter were obtained by mixing meta kaolin, supplied by Personal Factory Spa (Simbario, Italy) and an activating solution prepared from sodium silicate supplied by Sasol Italy SPA (Milan, Italy), sodium hydroxide (Sigma Aldrich) and water, in quantities sufficient to obtain a solid / water ratio of 0.51 in the finished product, a  $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$  ratio of 1 and a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio of 3.8. During the mixing phase a quantity of 5A zeolite equal to 5% by weight on the metakaolin was added to the system (figure 1a). In order to accelerate the geopolymerization reaction, the pastes were sealed and placed in the oven at 50 °C for an hour and then allowed to mature at room temperature for 7 days. The geopolymer was obtained as a monolithic piece (figure 1b), therefore before its use in experimentation, it was finely ground into a mortar mill in order to increase its active surface (figure 1c).



**Figure 1.** (a) Initial geopolymeric paste; (b) geopolymer; (c) pulverized geopolymer.

After pretreating the zinc ferrite and synthesizing the geopolymer, two aqueous systems were prepared, the first containing zinc ferrite and geopolymer e while the second containing only geopolymer. The latter was used as blanc during analytical measurements to take into account any releases of some metals by the geopolymer. The following table 1 shows the proportions by weight of the systems used.

**Table 1.** Proportions by weight of the aqueous system used.

System	Zinc ferrite (g)	Geopolymer (g)	H <sub>2</sub> O (g)
Zinc Ferrite/Geopolymer	5	10	100
Blanc	---	10	100

In particular, the zinc ferrite was added directly in water, while the geopolymer was previously inserted in a filter paper bag and kept suspended in the solution (figure 2a, b), to allow at the end of the release tests an easy separation of the geopolymer from the system.

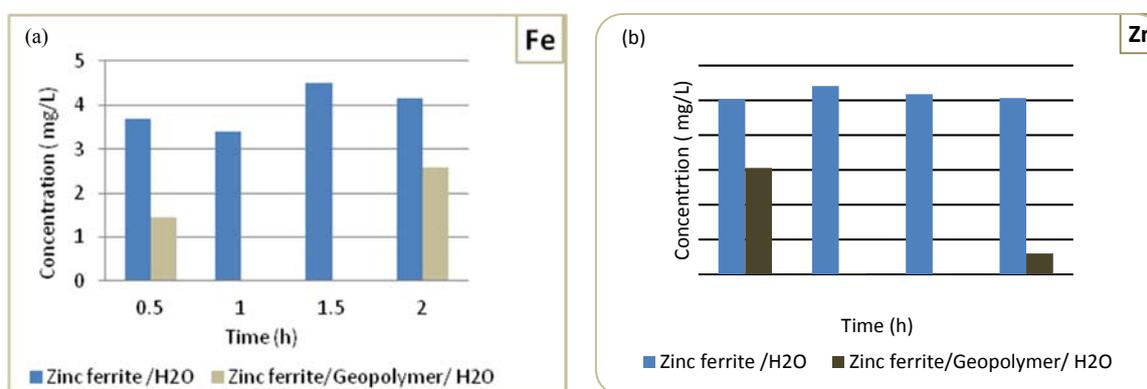


**Figure 2.** (a) Filter paper bag containing the geopolymer; (b) aqueous system: Geopolymer/Zinc ferrite; (c) filtered solution after release tests.

All systems were kept stirring at room temperature. The tests were repeated varying the stirring times equal to: 0.5, 1, 1.5, 2 hours. At the end of the programmed times, each system was filtered and the resulting solution (figure 2c) was analyzed through a mass spectrometer (ICP-MS) which allowed to follow the concentration variations of some elements such as: Fe, Zn, Pb, Mn, Mg and Na as contact times vary.

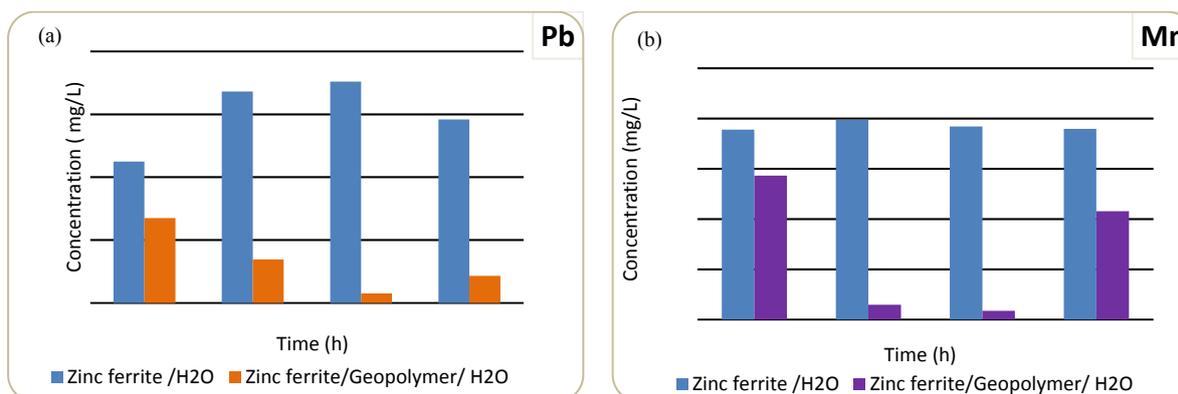
### 3. Results and discussion

The following graphs show the concentration of some elements released by zinc ferrite in the aqueous systems containing the geopolymer when the stirring times vary. In each graph, the data obtained are compared with those reported in a previous work [21], relating to the aqueous system containing only zinc ferrite. The data reported in figure 3a show how the geopolymer acts effectively on the abatement of the iron concentration.



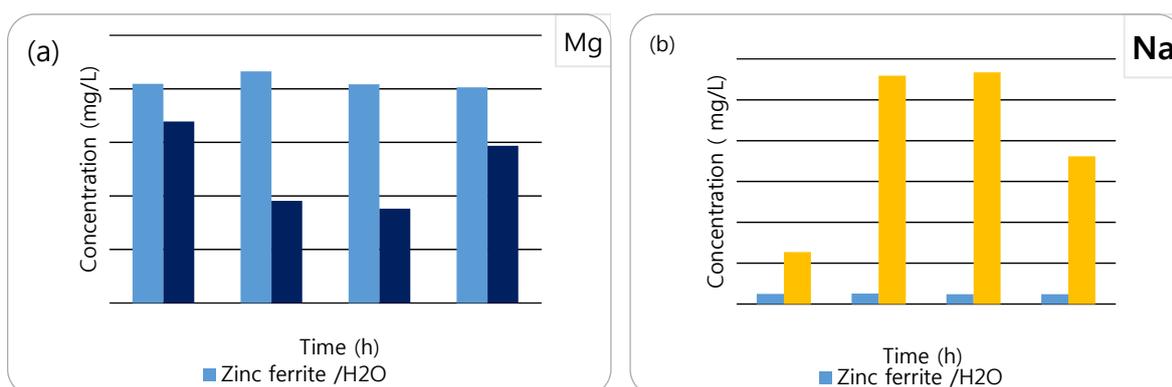
**Figure 3.** Variation of the concentration of Fe and Zn as a function of the stirring time for the aqueous system containing geopolymer/zinc ferrite and for the aqueous system containing only zinc ferrite [21].

After half an hour of contact there is a reduction of the Fe-concentration of over 60%, to reach an almost total reduction to an hour. The increase in concentration that occurs after two hours can be attributed to the particular and complex system of zinc ferrite, where for these times of agitation there is the probable descent into the field of other elements which are solubilized and which compete with iron on the exchange by the geopolymer. The data on Zinc (figure 3b) show a trend of variation of concentrations very similar to that of iron. After about half an hour of contact there is a reduction in the concentration of zinc of about 40% followed by a reduction close to 100% at an hour of agitation. At about two hours there is a slight increase in concentration, confirming in this case the thesis described above. The geopolymer also shows an effective role in the abatement of Pb (figure 4a) although for longer times than the two cases previously discussed. After an hour and a half there is a reduction of about 95%.



**Figure 4.** Variation of the concentration of Pb and Mn as a function of the stirring time for the aqueous system containing geopolymer/zinc ferrite and for the aqueous system containing only zinc ferrite [21].

An efficacy on the part of the geopolymer, very similar to that on the Pb, occurs in the case of Mn (Fig. 4b) where even for this element, at an hour and a half, the concentration is reduced by about 95%. In the case of magnesium (figure 5a), there is instead a lower efficacy of the geopolymer, in fact the best reduction does not exceed 60%, which occurs at about an hour and a half.



**Figure 5.** Variation of the concentration of the Mg and Na as a function of the stirring time for the aqueous system containing geopolymer/zinc ferrite and for the aqueous system containing only zinc ferrite [21].

The figure 5b shows the data related to the sodium concentration in the analyzed systems. It is possible to observe how the concentration of sodium increases with increasing agitation time and furthermore it is much higher than the zinc ferrite only system. All this evidently demonstrates the action of the geopolymer which exchanges the sodium ion in favour of other elements. At two hours, on the other hand, there is a slight decrease in the sodium concentration which is in perfect agreement with the decrease in the abatement of the elements analyzed, demonstrating that for these times of agitation the system becomes particularly detrimental to ion exchange.

From the set of data reported in all the previous graphs it is possible to deduce a common trend for all the analyzed elements: an hour and a half of agitation time is the optimal one to have the best reduction. After this time all the elements recorded a decrease in their concentration which confirms that after two hours of agitation there are important solubilization reactions by zinc ferrite components that create a crowding of elements released in the system giving rise to competitive phenomena between the elements and occlusion of the porous matrix of the geopolymer with reduction of the exchange action.

#### 4. Conclusion

The set of results obtained showed that geopolymers can be advantageously used in the removal of elements released in water from zinc ferrite.

In particular, the geopolymer exhibits a constant behavior regardless of the metal analyzed. The highest felling has been recorded for treatment times of 1 and 1.5 hour. Iron and zinc were almost completely removed after an hour of treatment, followed by Mn and Pb with a 95% removal at an hour and a half. Lower abatement rates were recorded for Magnesium. Finally, it is possible to conclude that the geopolymer used has shown particular efficacy to remove Fe, Zn, Mn, and Pb.

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