Removal of arsenic from water solutions by naturally occurring limonite

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Technical University of Crete

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Technical University of Crete

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Removal of arsenic from water solutions by naturally occurring limonite

E.Th. Stamboliadis, O. Pantelaki and E. Manutsoglu
Department of Mineral Resources Engineering, Technical University of Crete, Hania, Greece

N. Svanas
TVX Hellas, Greece

ABSTRACT

Arsenic is a pathogenic element and its presence in drinking water is undesirable. It is well known that arsenic reacts with iron to form insoluble substances and it is absorbed from water by iron compounds. This work examines the possibility to remove arsenic from water solutions by naturally occurring limonite.

Limonite samples were collected from an old iron ore mining area in the district of Hania in the island of Crete and one of them was selected for the experimental work. Two series of absorption tests were performed in order to develop an efficient procedure of arsenic removal from artificial water solutions of different concentrations.

In the first series of tests a constant amount of limonite is used in each case to remove arsenic from water solutions of the same volume that differ in the initial concentration of arsenic. For high initial concentrations of arsenic up to 2000 ppb the remaining arsenic is still high and the efficiency of the process is low. This problem is overcome in the second series of tests where the solid absorbent is added in stages and the overall efficiency of the process is increased. The remaining arsenic in the final water solution is lower and the total time of reaction is shorter than before.

These preliminary results have provided the background for a new series of research work that goes on and aims to develop a low cost commercial process, easy to handle, with acceptable quality of drinking water and high efficiency of absorbent.

1. INTRODUCTION

The presence of arsenic in drinking water causes many diseases in the human body and the prolonged usage of this water can be fatal. It is well known that iron compounds can react with arsenic in water and form insoluble precipitates leaving a clean water solution (Zhang *et al*., 2004). It is also known that solid substances containing iron compounds can absorb arsenic from water solutions. A large number of simple and also sophisticated techniques have been developed to remove arsenic from drinking water (Katsoyiannis *et al*., 2002; Meladiotis *et al*., 2002).

The present work tries to find the advantages and restrictions imposed by the use of naturally occurring iron minerals such as limonite in the process of arsenic removal from water solutions. Limonite was chosen for many reasons:

- It is a naturally occurring iron mineral, available at low cost,
- It exists in geological structures present in many geographical areas on earth,
- It is very reactive compared to other iron minerals due to its crystal water,
- It has a very large specific area available for absorption.

Two series of absorption tests were performed in order to develop an efficient procedure of arsenic removal from artificial water solutions of different concentrations.

In the first series of tests a constant amount of limonite (1 g) was used in each case to remove arsenic from water solutions of the same volume (1 liter) that differ in the initial concentration of arsenic. Three levels of initial arsenic concentration were used, namely

500 ppb, 1000 ppb and 2000 ppb. For high initial concentrations of arsenic up to 2000 ppb the remaining arsenic in the final solution is still high.

This problem is overcome in the second series of tests where the solid absorbent is added in stages and the overall efficiency of the process is increased. The remaining arsenic in the final water solution is lower and the total reaction time is reduced.

These preliminary results have provided the background for a new series of research work that goes on and intends to develop a low cost commercial process, easy to handle, with acceptable quality of drinking water and high efficiency of absorbent. The main restriction in this procedure is the filtration of the final solution for the removal of the suspended solids of limonite that have absorbed the arsenic. In the present work this problem was overcome by centrifuging the final solution but a more simple technique is examined for the development of a commercial process.

2. OCCURRENCE OF LIMONITE

Ferruginous stockworks and limonites occur in the Phyllite-Quartzite-Group within cataclastic shear zones of diverse thickness The lithological monotonous Phyllite Quartzite Group, is definitely the first allochthonous element of the island and is dominant in western Crete. It is characterized by an alternation of meta-graywackes, meta-sandstones and meta-pelites. Subordinately meta-basalts, mud-supported conglomerates and thin limestone or marble layers occur.

High concentrations of hematite and limonite, varying from a few mm up to 50 cm occur especially on contacts between quartzites, phyllites and marbles. (Dornsiepen and Manutsoglu, 1994). These bodies were the subject of mining for iron ore up to 1962 in west Crete.

Limonite is not a true mineral but a mixture of fine-grained iron oxides, generally dominated by goethite, but also possibly containing hematite, lepidochrocite and other minerals. Limonite forms mostly in or near oxidized iron and other metal ore deposits, and as sedimentary beds. It is a useful field term, and has been frequently reported in the literature.

Goethite (α-FeOOH) is the second most common naturally occurring iron oxide mineral after hematite and has been reported to be effective for arsenic adsorption (Zhang *et al*., 2004).

3. EXPERIMENTAL PROCEDURE

The experimental work is divided in three steps. In the first step it was necessary to find the appropriate samples of limonite and develop a procedure for their preparation before use. Three different samples, 5 kg each, were dried and crushed in a laboratory jaw crusher at minus 4 mm. Two kg of the crushed material was wet ground in a laboratory rod mill for 10 min at 60% solids. The mill product was classified by a water cyclone, while the cyclone products were dewatered and dried. The cyclone overflow was taken as the final sample. These samples were tested by X-ray diffraction to examine their mineralogical composition and assayed for the determination of the chemical composition. The main physical properties measured are the size distribution by a laser beam analyzer and the specific surface area using the B.E.T. technique. This property was used as the final criterion for the selection of the best sample.

The second experimental step was the study of the absorption of arsenic from water solutions by the limonite sample that was added to the solution in the form of suspended powder. In every test the volume of the solution used was 1 liter and the concentration of arsenic was adjusted by the addition of a concentrated solution of Arsenic Pentoxide ($As_2O_5.2H_2O$) in distilled water. Three levels of arsenic concentrations were prepared for the tests namely 500 ppb, 1000 ppb and 2000 ppb. The solution was continuously agitated and 1 g of the limonite sample was added. At specified time intervals a 20 ml sample was taken from the solution and prepared for the determination of the arsenic concentration. The main objective of the preparation is the filtration of suspended solids and the recovery of a solids free solution. The filtration by filter paper was a difficult task because the suspended solids were very fine. The technique finally adapted for the solid liquid separation was the centrifuge. After the final sample was taken the agitation was stopped and the solids were allowed to settle

overnight and a clean solution was decanted from the settled solids.

During the third experimental step the absorption process was slightly modified and the solid absorbent was added at stages (1 g at each stage) at predetermined time intervals of 10 min after the collection of the solution sample that corresponds at the end of the previous stage. The rest of the technique is the same as in the second step.

The assays of the liquid samples collected during the test work were performed at the chemical laboratory of TVX Hellas in Stratoni, Chalkidiki using the atomic adsorption method.

4. TEST RESULTS

4.1 Preparation and selection of the absorbent

Samples of limonitic material were taken from three neighboring locations in the area of Cliaron Village of Hania, Crete. Each sample was crushed to –4 mm and homogenized. The representative samples were assayed by atomic adsorption tested for the mineralogical composition by X-ray diffraction.

The mineralogical composition is more or less the same for all three sample and contains

- goethite,
- quartz,
- muscovite, and
- carbonates, mainly calcite and dolomite.

The chemical analysis is presented in Table 1. Each sample was wet ground for 10 min in a laboratory rod mill D x L = 200 x 300 mm with 8.5 kg rod load. The mill feed was 2 kg of solids plus 1.5 liters of water. The mill product was classified in a 2" hydro cyclone at a cut size about 10 microns. The cyclone overflow (O/F) was tested for its specific surface by the method of B.E.T. and for its size distribution by a laser beam size analyzer. The

Table 1: Chemical analysis per cent.

Sample	MP 478	MP 479	MP 480
Fe_2O_3	42.89	15.78	35.74
SiO_2	33.54	62.04	37.65
Al_2O_3	11.49	14.44	12.70
cr. H_2O	8.33	4.73	9.47
CaO	0.92	0.38	0.61
MgO	0.40	0.60	2.06
CO_2	1.72	1.47	1.03

Table 2: Physical properties.

PROPERTY	Sample		
	MP478	MP479	MP480
Moisture, %	3.47	0.29	4.17
O/F, weight %	24.95	23.35	46.14
S.S.A. m^2/g	19.6	8.9	48.8
Cr. H_2O, %	8.33	4.73	9.47

cyclone O/F is the material to be used for the absorption tests and its settling rate in water was also measured using a 1-liter volumetric cylinder.

The physical properties of the three samples are presented in Table 2. The sample selected is the MP 480 because it gives high weight % recovery its has higher amount of crystal water that influences the activity of Fe_2O_3 and also has the largest specific surface area.

4.2 First series of absorption tests

In the first series of absorption tests the absorbent (1 g of limonite) was added in 1 liter solution of preset arsenic concentration and was agitated continuously while samples of the solution were taken at predetermined time intervals and analyzed for arsenic. Figure 1 presents the drop of As content of the water solution versus time for three different levels of initial arsenic concentration. Figure 2 presents the amount of As absorbed per gram of solids. In the beginning there is a rapid absorption that slows down as time passes and appears to tend to a maximum value. The curves of Figure 2 can be transformed to straight lines as follows.

Let $F(t)$ the amount of arsenic absorbed per unit weight of solids (µg/g), where t the time in minutes. Consider also Fm the maximum value
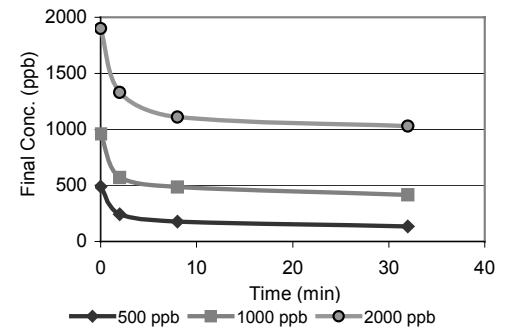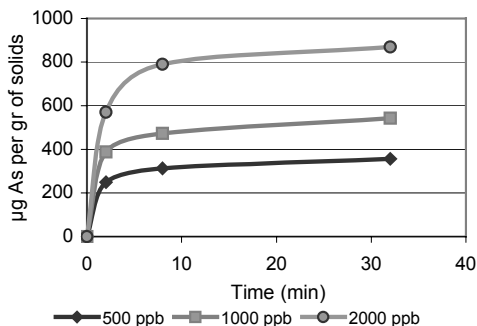

Figure 1: Final Concentration of Water Solution

Figure 2: Total mass removed.

where $F(t)$ tends. Then one can describe the curves of Figure 2 by equation (1):

$$\frac{F(t)}{t} = k \cdot [F_m - F(t)] \qquad (1)$$

The constant k determines the rate of absorption. Equation (1) is transformed to (2) by mathematical manipulation:

$$\frac{t}{F(t)} = \frac{t}{F_m} + \frac{1}{k \cdot F_m} \qquad (2)$$

The plot of equation (2) is a straight line presented in Figure 3, with slope $1/F_m$ and intercept $1/kF_m$. The values of k and F_m are calculated from Figure 3 and present in Table 3. It appears that the value of k is practically the same for all three cases while F_m depends on the initial concentration of arsenic.

    The final conclusion from this series of tests is that:

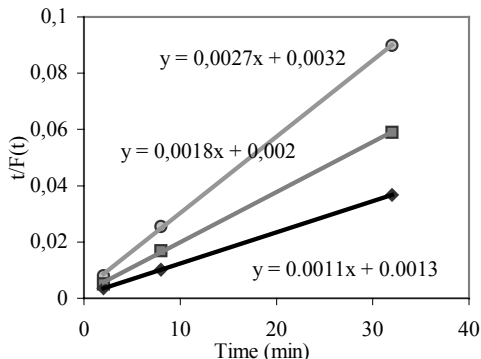- the remaining concentration of As is still high and

Table 3: Values of k and F_m

As, ppb	k	F_m
500	1.19	370
1000	1.12	555
2000	1.18	909

- the rate of concentration decrease is faster during the first minutes of the test.

4.3 Second series of absorption tests

The second series of tests was designed to reduce the concentration of arsenic in the final solution even further. For this purpose one can take advantage of the fact that the absorption rate is faster in the first minutes and add an extra amount of the absorbent after the first addition has absorbed most of the initial arsenic in the solution.

    The procedure chosen is to sample the solution every 10 minutes and successively add 1 g of solids each time. Figure 4 shows the final concentration of arsenic versus time for three initial concentrations. In this test the final concentration drops at much lower levels and for initial concentrations bellow 500 ppb the final one is acceptable for drinking water.

    Due to the successive additions of solids the total absorption density drops as more solids are added shown in Figure 5. Here comes the advantage of using a low cost naturally occurring absorbent such as limonite.

5. DISCUSSION

The absorbent used to remove arsenic from water solutions is a naturally occurring raw material abundant in may geographical areas of
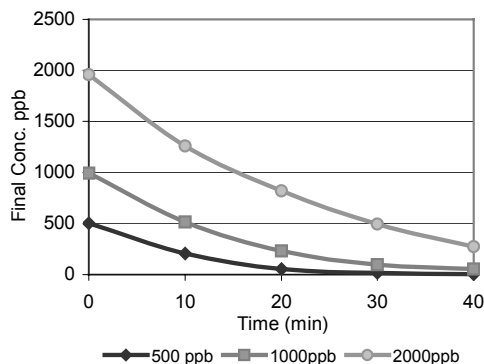

Figure 3: Transformed absorption curve.

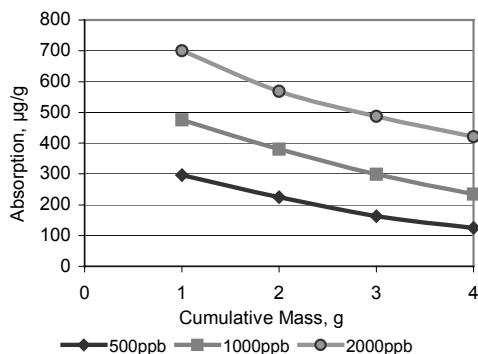Figure 4: Final concentration of water solution.

Figure 5: Total absorption density.

the world.

The absorption technique used in stirred vessels is simple and can handle large quantities of water necessary for urban areas. The main difficulty of the technique, as mentioned in the beginning, is the solid liquid separation due to the low settling rate of the finest particles of the solids. The settling rate becomes slower after the absorption of arsenic from the solution and is probably due to the charge that the solids acquire. Centrifugal forces can be used as it was done in the present work and are also applicable in industrial scale.

The absorption is faster in the beginning and slows down as the arsenic concentration drops with time. The absorption density tends to a maximum and the curves can be treated mathematically using the equation (1). From these curves one can calculate the maximum absorption density F_m as well as the rate constant k. From the experimental data obtained it seems that, Fm increases proportionally to the initial concentration but k is practically constant.

The initial levels of As used are above the ones, usually found in waters for urban consumption, and the final concentrations are still high although a significant amount of arsenic has been removed from the solution. The final concentration of arsenic can be further reduced in sorter time by successive addition of the absorbent in time interval when the reaction rate is still high. The result is an acceptable drinking water quality for waters with initial concentration bellow 500 ppb, which is the usual case.

The advantage of using a low cost naturally occurring material, like limonite, is obvious and

the technical parameters involved in the application are within the present technological experience.

6. CONCLUSIONS

The main conclusions can be summarized in the following list:

- Limonite can be used for the removal of arsenic from drinking water.
- It is a low cost naturally occurring material, found in many parts of the world.
- The technique used, in stirred open vessels, can handle large quantities of water.
- The technology required for solid liquid separation is available.
- The quality of the final water improves if the absorbent is added in time intervals when the reaction rate is still high.
- Drinking water quality is obtained from initial solutions with as high initial concentrations as 500 ppb of arsenic.

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