

# IDENTIFICATION OF IRON CORROSION PRODUCTS IN ARSENIC REMEDIATION USING ZERO VALENT IRON

K. TYROVOLA<sup>\*</sup>, N.P. NIKOLAIDIS<sup>\*</sup>, J.J. OJEDA<sup>\*\*</sup>, M.E. ROMERO-GONZÁLEZ<sup>\*\*</sup>, S.A. BANWART<sup>\*\*</sup>

*<sup>\*</sup>Technical University of Crete, Department of Environmental Engineering, 73100 Chania, Greece*

*<sup>\*\*</sup>Cell-Mineral Research Centre. Kroto Research Institute, University of Sheffield, Broad Lane, Sheffield S3 7HQ*

**SUMMARY:** The objective of this study was to identify the corrosion products which are formed onto the surface of Zero Valent Iron (ZVI) during arsenic removal from geothermal groundwaters and to clarify the role of the corrosion products in the mechanism of arsenic removal. The results of this study demonstrated that carbonate green rust was formed onto the surface of ZVI during short and long term column experiments. In addition, As(V) was mainly reduced to As(III) onto the surface of ZVI. A small amount of As(III) was oxidized to As(V) and that was attributed to the formation of carbonate green rust and other corrosion products on the surface of ZVI.

## 1. INTRODUCTION

The finding that groundwater from large areas all over the world is enriched with arsenic (As), has increased the number of studies dealing with arsenic removal. Arsenic is a highly toxic and carcinogenic element which can be released to groundwater through natural processes and anthropogenic activities. The predominant species of arsenic in soil and natural waters are the inorganic arsenic As(III), and As(V) (Smedley and Kinniburgh, (2002). Due to the adverse health effects that occur from the consumption of arsenic contaminated water there is a very strict maximum contaminant level (MCL) for arsenic in drinking water ( $10 \mu\text{g l}^{-1}$ ). Numerous technologies have been developed in order to remove arsenic from water. Zero valent iron (ZVI) is considered to be a potential, low cost remediation agent for the efficient removal of arsenic (Lackovic and Nikolaidis, 2000, Nikolaidis et al, 2003, Nikolaidis and Tyrovola, 2006). Arsenic removal mechanism by ZVI involves the formation of Fe(II) and Fe(III) corrosion

products onto the surface of iron due to oxidation. The formation of various corrosion products on the surface of ZVI results in the creation of adsorption sites for both As(III) and As(V). The suggested mechanism of arsenic removal is the formation of inner-sphere bidentate As(III) and As(V) complexes on iron corrosion products (Manning et al, 2002). In addition, other studies suggest that surface precipitation is the predominant removal process of arsenic by ZVI (Lackovic and Nikolaidis, 2000, Nikolaidis et al, 2003).

The objective of this study was to identify the corrosion products formed onto the surface of ZVI during arsenic removal from groundwater and to clarify the role of the corrosion products in the mechanism of arsenic removal. Specifically, the goals of this study were: i) to conduct short and long term column experiments with arsenic (As(III) and As(V)) contaminated groundwater from geothermal regions, ii) to characterize ZVI's corrosion products, after the completion of the column experiments, using spectroscopic techniques such as FTIR and XRD and iii) to examine arsenic speciation onto the surface of ZVI using XPS. In particular, arsenic removal in column experiments was conducted in the laboratory with synthetic water representing the geochemistry of the geothermal groundwater of Triglia-Petralona. Triglia is a town in Western Chalkidiki. Arsenic contamination in Triglia is originated from the Katsika area's karstic geothermal water with temperature varying from 29 to 41<sup>0</sup>C (Tyrovola et al, 2006). The concentration of arsenic in geothermal water varied from 1000 to 4000 µg AsL<sup>-1</sup>.

## 2. METHODOLOGY

ZVI was obtained from Connelly-GPM, Inc. (Chicago, IL). ZVI was sieved to constrain the grain size from 0.300 to 1.180 mm with a mean surface area of 2.67 m<sup>2</sup> g<sup>-1</sup>, determined using the BET method. The silica sand used for all columns had size fraction from 0.50 to 1.40 mm with dry bulk density of 1.19 g ml<sup>-1</sup>. Arsenic stock solutions (1000 mgAsL<sup>-1</sup>) were prepared from reagent grade Na<sub>2</sub>HAsO<sub>4</sub> · 7H<sub>2</sub>O (Fluka) and NaAsO<sub>2</sub> (Fluka) for As(V) and As(III), respectively with ultra pure water. Synthetic groundwater was prepared in the laboratory as described by Tyrovola et al. (2006). The pH of the synthetic water was adjusted around 7.0 by addition of small amounts of H<sub>2</sub>SO<sub>4</sub>. The synthetic groundwater was purged with He in order to remove the dissolved oxygen. The experimental part of this work was comprised by six column experiments as shown in Table 1. Columns I –IV were run for long period of time while columns V, VI were run for only 7 days. The columns were designed for saturated flow in an upward configuration in order to prevent air entrapment between sand and iron grains. Columns were run using a Watson Marlow peristaltic pump with flow rate of about 0.66 ml min<sup>-1</sup> yielding a hydraulic retention time of 10 minutes. The columns were made of plexiglass and were packed with 15 g of ZVI and 15 g of silica sand (1:1 w:w) having a porosity value of 0.42. Glass wool was placed at both ends of the columns. Samples were taken periodically from the column effluent and influent, filtered with a nylaflo membrane 0.2 µm filter, acidified with HNO<sub>3</sub> and preserved at 4 <sup>0</sup>C before arsenic analysis. Chemical analysis of arsenic in columns was conducted by anodic stripping voltammetry with Nano Band<sup>TM</sup> Explorer system. This method was used for the determination of free dissolved As(III). Total arsenic analysis was conducted after the addition of 0.5 N

thiosulfate solution (reducing agent) in the sample in order to covert all inorganic arsenic to As(III). The detection limit of this method was 5  $\mu\text{g As l}^{-1}$

### 3. SPECTROSCOPIC STUDIES

After the completion of the experiments, the columns were disassembled and the media (ZVI and sand) was removed from the columns in an anaerobic chamber under nitrogen atmosphere. The media was then separated in three parts: a, b, c by cutting it into sections of approximately 3.3 to 3.5 cm. Each part was separated into the Fe –section and the sand section by a magnet. Bulk mineralogy of the material was determined by X-ray diffraction (XRD), using a Siemens D500 XRD operating at 35 kV and 35 mA, with a graphite monochromator, and CuK $\alpha$  radiation. A 0.02°  $\theta$  scan step and 1-s scan time per step was used. FTIR analysis was conducted using the Perkin-Elmer Spectrum One FTIR Spectrometer using KBr pellets. For each sample 100 scans were collected at a resolution of 4  $\text{cm}^{-1}$ . The media was also analyzed on a KRATOS AXIS 165 Ultra Photoelectron Spectrometer operated at 15KV and 10mA using the Al K(alpha) X-ray source (1486.6 eV). The takeoff angle was fixed at 90 degrees. On each sample the data was collected from two randomly selected locations, and the area corresponding to each acquisition was 400 $\mu\text{m}$  in diameter. Each analysis consisted on a wide survey scan (pass energy 160eV, 1.0eV step size) and high-resolution scan (pass energy 20eV, 0.1eV step size) for component speciation. The binding energies of the peaks were determined using the C 1s peak at 284.5 eV. The software CasaXPS 2.3.12 was used to fit the XPS spectra peaks.

Table 1. Column Characteristics.

	Column I	Column II	Column III	Column IV	Column V	Column VI
Inner diameter (cm)	1.4	1.4	1.4	1.4	1.4	1.4
Column length (cm)	10.6	10.3	10.6	10.7	10.0	10.0
Bed Volume ( $\text{cm}^3$ )	16.324	15.862	16.324	16.478	15.4	15.4
Porosity	0.42	0.42	0.42	0.42	0.42	0.42
Pore Volume ( $\text{cm}^3$ )	6.86	6.66	6.86	6.92	6.47	6.47
Hydraulic Retention Time (min)	10	10	10	10	10	10
Flow rate( $\text{mL}/\text{min}$ )	0.686	0.686	0.686	0.686	0.647	0.647
Arsenic Speciation in the inflow	As(V)	As(III)	As(V)	As(III)	As(III)	As(V)
Temperature ( $^{\circ}\text{C}$ )	20	20	40	40	20	20
Initial arsenic concentration ( $\mu\text{gL}^{-1}$ )	2000	2000	2000	2000	2000	2000
Time of operation (days)	272	272	272	57	7	7

## 4. RESULTS AND DISCUSSION

### 4.1 Flow Rate- Hydraulic Retention Time

Columns I, II and III were run in parallel for 272 days, while column IV was operated for 57 days. Columns I, II, III and IV were designed to be operated with 10 minutes hydraulic retention time thus the flow rate of these columns was initially set to 0.66  $\text{mL min}^{-1}$ . The flow rate in Column I and II had similar trend (data not shown). Specifically, the flow rate in Column I and II

was constant till the 138<sup>th</sup> day and the 143<sup>rd</sup> day, respectively. The average flow rate, for column I till the 138<sup>th</sup> day was 0.69 mL min<sup>-1</sup> and the average flow rate for column II till the 143<sup>rd</sup> day was 0.73 mL min<sup>-1</sup>. After the 138<sup>th</sup> day in column I and after the 143<sup>rd</sup> day in column II, the flow rate started to decrease exponentially with time. The decrease in flow rate was caused due to clogging. The flow rate in Column III was constant during the experiment (272 days). The average flow rate was 0.64 mL min<sup>-1</sup>. In addition, the flow rate in Column IV was constant for the time of operation (57 days). The operation of this column was interrupted because of leakage. The flow rate had an average value of 0.70 mL min<sup>-1</sup>. Columns I, II, and IV were stopped due to clogging. This happened because it was difficult to achieve reducing/anoxic conditions in the feeding solution despite of being purged with helium. In addition, due to the low flow rates, air could get into the tubing where iron precipitation was observed.

## 4.2 Arsenic behaviour

Columns I and II were run in parallel at 20 °C in order to compare As(V) and As(III) removal, respectively. The concentration of As(V) in the inlet of column I ranged from 1871 µg L<sup>-1</sup> to 2233 µg L<sup>-1</sup> with average arsenic concentration at 2032 µg L<sup>-1</sup>. In addition the average concentration of As(III) in column II was 2022 µg L<sup>-1</sup> ranging from 1833 to 2207 µg L<sup>-1</sup>. As shown in Figure 1 (a) and (b) the profile of arsenic concentration in the effluent can be separated in three different time periods: 1) a start up period, 2) a subsequent period and finally 3) the clogging period. This trend has been reported in the literature previously (Lackovic, et al, 2000). The start-up period lasted for 82 days and 65 days for columns I and II, respectively. The subsequent period started from the 83<sup>rd</sup> till the 153<sup>rd</sup> day for column I and from 65<sup>th</sup> till the 153<sup>rd</sup> day for column II. Finally, the clogging period followed the subsequent period till the interruption of the column operation. A start up period was needed in order to achieve lower concentrations of arsenic in the effluent (Figure 1 (a) and (b). The iron export from the columns due to corrosion (data not shown) increased during the startup period and then it was stabilized in the subsequent period, exhibiting a similar trend to the arsenic concentrations observed in the effluent of the columns. It is suggested, therefore, that this phenomenon was due to an increase in the reactive sites for surface precipitation/ co-precipitation caused by iron corrosion (Tyrovola et al., 2007). Finally, in the clogging period, the flow rate was very low, the concentration of iron decreased versus time (data not shown) and the concentration of arsenic increased with time. During the clogging period, precipitation of solids on the ZVI resulted on the reduction of the reactive sites on ZVI and therefore affected the capacity of arsenic removal (Phillips et al., 2000). In column III only two time periods were observed: the start up period, and the subsequent period. This column was operated contentiously at 40 °C with As(V) in the inlet and did not reach the clogging period. The concentration of As(V) in the inlet ranged from 1866 to 2232 µg L<sup>-1</sup> with average concentration of 2037 µg L<sup>-1</sup>. The total concentration of arsenic in the effluent ranged from 5 to 430 µg L<sup>-1</sup>. In column IV only the start up period was observed. Column IV was operated only for 57 days at 40 °C with As(III) in the inlet and its operation was interrupted due to leakage. During its operation, the average concentration of arsenic in the inlet was 1994 µg L<sup>-1</sup> ranging from 1890 to 2227 µg L<sup>-1</sup>, while the average concentration of arsenic in the outlet was 328 µg L<sup>-1</sup> ranging from 9 to 587 µg L<sup>-1</sup>. The column work demonstrated that the

ZVI used is capable to remove As(V) more effectively than As(III) under the same conditions at the same temperature (20<sup>0</sup>C). This has been also reported in the literature with the same type of ZVI (Lackovic et al, 2000, Tyrovolas et al, 2006). A temperature effect was also observed. Greater removal was achieved for As(V) at 40<sup>0</sup>C (32.0 mgAs/g Fe) than at 20<sup>0</sup>C (24.2 mgAs/g Fe). Unfortunately, column IV was operated for a small period of time making the assessment of the effect of temperature on As(III) removal difficult.

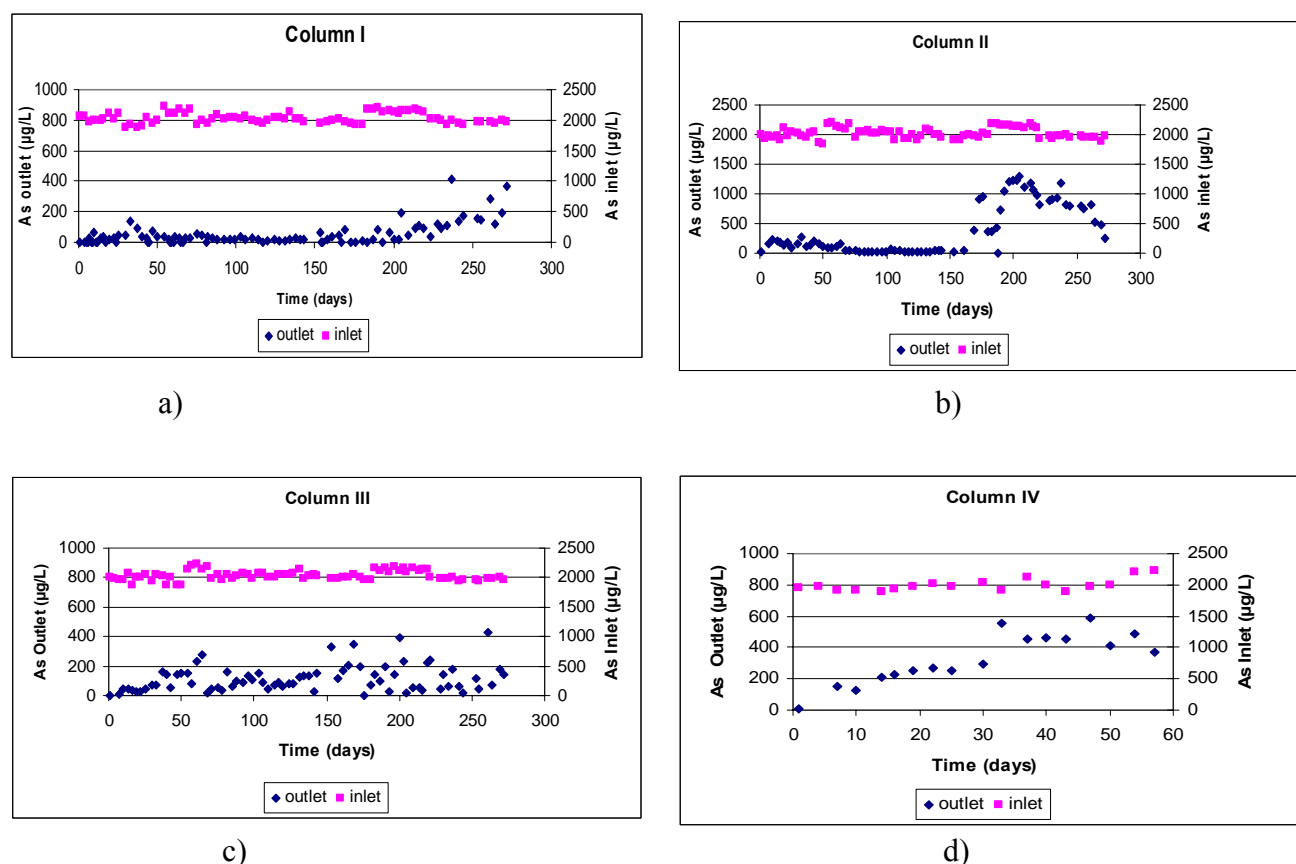


Figure 1. Arsenic concentration for columns I -IV. a) Column I: As(V) @ 20<sup>0</sup>C, b) Column II: As(III) @ 20<sup>0</sup>C, c) Column III: As(V) @ 40<sup>0</sup>C, d) Column IV: As(III) @ 40<sup>0</sup>C.

### 4.3 Spectroscopic results

The FTIR spectra shows three main regions as described also by the work of Su and Puls (2004) and Taylor (1980). The stretching region of the O-H bonds from 4000 to 2000 cm<sup>-1</sup>, the combination band and the overtone region from 2000 to 1200 cm<sup>-1</sup> and the lattice mode and molecular anion region from 1200 to 400 cm<sup>-1</sup> which contains peaks related to the lattice Fe-OH modes (Legrand et al., 2003, Su and Puls, 2004). The spectra of the first part (a) of column I is presented in Figure 2(a). Each spectra has a peak at 1350-1354 cm<sup>-1</sup> that is assigned to carbonate green rust (CGR) (Su and Puls, 2004, Legrand et al., 2003). In addition, at the lattice mode and molecular anion region we can see a peak at 780 cm<sup>-1</sup> which is attributed to goethite and a peak at 670 cm<sup>-1</sup> for magnetite (Lakshminathiraj et al., 2006). The spectra of Columns V, VI were collected after 7 days of operation and it is considered a fresh sample. There is a small peak at

1350-1354  $\text{cm}^{-1}$  characteristic of the carbonate green rust. In addition there is a peak at 780  $\text{cm}^{-1}$  which is assigned to goethite.

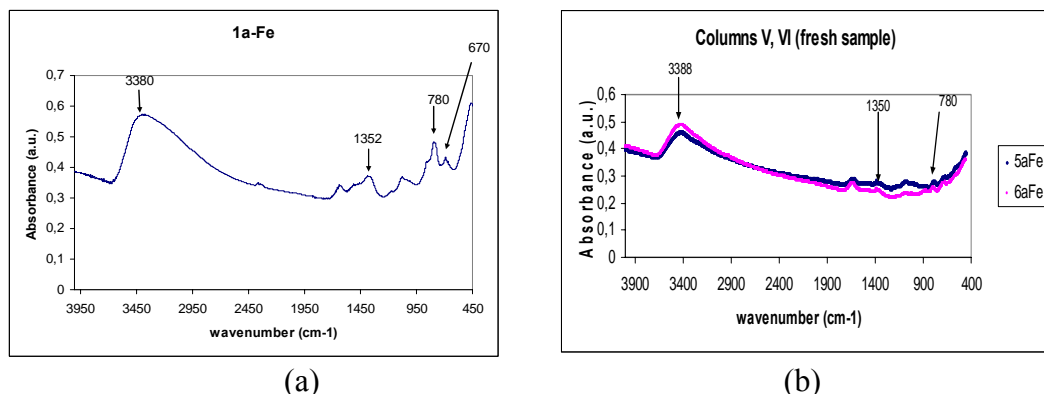


Figure 2. FTIR scans. (a) FTIR scan of column I, (b) FTIR scans for Columns V, VI.

The XRD results showed that all samples had a similar mineral composition. The major phases are siderite, carbonate green rust (CGR), magnetite, ferrihydrite, maghemite and goethite. Quartz was also found indicating an inefficient procedure for the separation of the Fe –section and the sand section. From the XPS analysis, the different arsenic species present in the column were characterised based on the binding energies of the As species present on the influent solutions. The Binding Energy for As(V) in  $\text{Na}_2\text{HAsO}_4$  is at 45.5 eV (Bang et al., 2005, Costa, et al., 2002). The Binding Energy for As(III) in  $\text{NaAsO}_2$  is at 44.2 and for As(0) is at 41.5. Some shifts can be observed in As 3d BEs in different arsenic species:  $\text{BE}(\text{AsO}_4^{3-}) = 44.9$  eV,  $\text{BE}(\text{HAsO}_4^{2-}) = 45.5$  eV,  $\text{BE}(\text{H}_2\text{AsO}_4^-) = 46.7$  eV (Bang et al., 2005). The XPS spectra of the columns I, III, VI (in which the influent water contained only As(V)), shows a peak attributed to As(III). This occurs due to the reduction of As(V) to As(III) by Fe(0) on the ZVI. The XPS spectra of the columns II, IV, V (in which the influent water contained only As(III)), shows a peak attributed mainly to As(III) in one broad peak. However, since the obtained peak was very broad, a smaller portion may be attributed to As(V), indicating a partial oxidation of As(III) to As(V) on the surface of ZVI. The possibility of the oxidation of As (III) to As(V) is complemented by the previously observed oxidation products CGR,  $\text{Fe}(\text{OH})_3$ , goethite, magnetite from the FT-IR and XRD analysis. Taking into account the identified products using X-ray and FT-IR spectroscopy the following chemical equations (see Table 2) are proposed for the transformation of As(III) and As(V) in the studied columns (Su and Puls, 2004).

## 5. CONCLUSIONS

The main conclusions of this work are:

- The formation of CGR observed in the columns that were operated for a long period of time and in the columns that were operated for a few days indicated that the formation of CGR is a fast process.
- The reduction of As(V) to As(III) on the surface of ZVI was observed under the proposed conditions.

- Adsorbed As(III) may be oxidised to As(V) over time. This was observed in the columns that were operated both for a long period of time and in the columns that were operated for a few days.

Table 2. Reactions- Mechanism of arsenic removal-iron corrosion.

Mechanism	Reaction
Anaerobic Iron Oxidation	$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$
Fe(OH) <sub>2</sub> Formation	$Fe^{2+} + 2OH^- \Leftrightarrow Fe(OH)_2$
Aerobic iron Oxidation- Fe(II) Formation	$2Fe^0 + 2H_2O + O_2 \rightarrow 2Fe^{2+} + 4OH^-$
Aerobic Oxidation of Fe(II) to Fe(III)	$4Fe^{2+} + O_2 + 2H_2O \Leftrightarrow 4Fe^{3+} + 4OH^-$
Formation of Fe(OH) <sub>3</sub> (s)	$3Fe^{3+} + 4OH^- \Leftrightarrow Fe(OH)_3$
Reduction of As(V) to As(III) from ZVI	$Fe^0 + HAsO_4^{2-} + 4H^+ \Leftrightarrow Fe^{2+} + H_3AsO_3 + H_2O$ $Fe^0 + H_2AsO_4^- + 3H^+ \Leftrightarrow Fe^{2+} + H_3AsO_3 + H_2O$
Formation of CGR	$4Fe^{2+} + 2Fe^{3+} + CO_3^{2-} + 14H_2O \Leftrightarrow$ $Fe(II)_4Fe(III)_2(OH)_{12}CO_3 \cdot 2H_2O + 12H^+$
Oxidation of As(III) to As(V) from CGR	$Fe(II)_4Fe(III)_2(OH)_{12}CO_3 + 9H^+ + H_2AsO_3^- \Leftrightarrow$ $\Leftrightarrow 6Fe^{2+} + HAsO_4^{2-} + CO_3^{2-} + 11H_2O$
Oxidation of As(III) to As(V) from Fe(OH) <sub>3</sub>	$2Fe(OH)_3(s) + 3H^+ + H_2AsO_3^- \Leftrightarrow$ $\Leftrightarrow 2Fe^{2+} + HAsO_4^{2-} + 5H_2O$
Oxidation of As(III) to As(V) from goethite	$\alpha - FeOOH(s) + 3H^+ + H_2AsO_3^- \Leftrightarrow 2Fe^{2+} + HAsO_4^{2-} + 3H_2O$
Oxidation of As(III) to As(V) from magnetite	$Fe_3O_4(s) + 5H^+ + H_2AsO_3^- \Leftrightarrow$ $\Leftrightarrow 3Fe^{2+} + HAsO_4^{2-} + 3H_2O$

## ACKNOWLEDGMENTS

This project was funded by the Hellenic Ministry of Education under the contract number MIS88744 - EPEAEK II-IRAKLITOS.

## REFERENCES

- Bang S., Johnson M.D., Korfiatis G.P., Meng X. (2005) Chemical reactions between arsenic and zero-valent iron in water. *Water Research*, 39(5), 763-770.
- Costa M.C. Botelho do Rego A.M., Abrantes L.M. (2002) Characterization of a natural and an electro-oxidised arsenopyrite: a study on electrochemical and X-ray photoelectron spectroscopy. *Int. J. Miner. Process*, 65, 83-108.
- Fairley, N. (2006) *CASA-XPS*, 2.3.12ed., Casa Software
- Lackovic J.A., Nikolaidis N.P., Dobbs, G.M. (2000) Inorganic Arsenic Removal by Zero-Valent Iron. *Environmental Engineering and Science*, 177 29-39.

- Lakshmipathiraj P., Narasimhan B.R.V., Prabhakar S., Bhaskar Raju G. (2006). Adsorption of arsenate on synthetic goethite from aqueous solutions. *Journal of Hazardous materials*, B136, 281-287.
- Legrand L., Maksoub R., Sagon G., Lecomte S., Dallas J.P. and Chausse A. (2003) Electroanalytical and kinetic investigations on the carbonate green rust-Fe(III) redox system. *Journal of the Electrochemical Society*, 150 (2), B45-B51.
- Manning B.A., Hunt M.L., Amrhein C., Yarmoff J.A. (2002) Arsenic (III) and Arsenic (V) reactions with zerovalent iron corrosion product. *Environ. Sci. Technol.* 36(24), 5455-5461.
- Nikolaidis N.P., Dobbs G.M., Lackovic, J.A. (2003) Arsenic Removal by Iron Filings: Field, Laboratory and Modeling Studies, *Water Research*, 37(6), 1417-1425.
- Nikolaidis N.P., Tyrovolas K. (2006) Removal of Arsenic from Groundwater – Mechanisms, Kinetics, Field/Pilot and Modeling Studies. In: Lo, I.M.C., Lai, K.C.K. (Eds.), *Zero-valent Iron Reactive Materials for Hazardous Waste and Inorganics Removal*, ASCE Publications, Reston, VA, Chapter 9, 151-164.
- Phillips D., Gu B., Watson D., Roh Y., Liang L. and Lee S. (2000) Performance Evaluation of a Zerovalent Iron Reactive Barrier: Mineralogical Characteristics. *Environ. Sci. Technol.* 34, 4169-4176.
- Smedley P.L., and Kinniburgh D.G. (2002). A review of the source, behaviour and distribution of arsenic in natural waters. *Applied Geochemistry*, 17, 517-568.
- Su C., and Puls R. W. (2004) Significance of iron (II,III) Hydroxycarbonate green rust in arsenic remediation using zerovalent iron in laboratory column tests. *Environ. Sci. Technol.*, 38(19), 5224-5231.
- Tyrovolas K., Nikolaidis N.P., Veranis, N., Kallithrakas-Kontos N., Koulouridakis, P.E. (2006). Arsenic removal from geothermal waters with zero-valent iron - Effect of temperature, phosphate and nitrate. *Water Research*, 40, 2375 – 2386.
- Tyrovolas K., Peroylakis E., Nikolaidis N.P. (2007). Modeling of arsenic immobilization by zero valent iron. *European Journal of Soil Biology* 43, 356-367.
- Taylor, R.M. (1980) Formation and properties of Fe(II)Fe(III) hydroxy-carbonate and its possible significance in soil formation, *Clay Minerals*, 15, 369-382.