



## ARSENIC REMOVAL FROM GROUNDWATER USING ZERO-VALENT IRON: PILOT APPLICATION IN GEOTHERMAL REGIONS

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### ABSTRACT

There is a great concern of arsenic contamination in drinking water around the world. Arsenic is a toxic metalloid that causes cancer. Recently the U.S. EPA , WHO and the European Commission have lowered the maximum contaminant level for arsenic (MCL) in drinking water from 50µg/L to 10µg/L. This paper presents the geothermal field in the region of Triglia Petralona (West Chalkidiki-Greece), the geochemistry of the region and also the effectiveness of a zero- valent iron technology in removing arsenic from the groundwater for drinking water. The technology can remove arsenic below the MCL.

## ΑΠΟΜΑΚΡΥΝΣΗ ΑΡΣΕΝΙΚΟΥ ΑΠΟ ΥΠΟΓΕΙΑ ΝΕΡΑ ΧΡΗΣΙΜΟΠΟΙΩΝΤΑΣ ΣΤΟΙΧΕΙΑΚΟ ΣΙΔΗΡΟ: ΠΙΛΟΤΙΚΗ ΕΦΑΡΜΟΓΗ ΣΕ ΓΕΩΘΕΡΜΙΚΕΣ ΠΕΡΙΟΧΕΣ

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### ΠΕΡΙΛΗΨΗ

Τα τελευταία χρόνια υπάρχει μεγάλο ενδιαφέρον σε όλον τον κόσμο για την ρύπανση του πόσιμου νερού από αρσενικό. Το αρσενικό είναι ένα τοξικό μεταλλοειδές που προκαλεί καρκίνο. Πρόσφατα η U.S. EPA, ο Παγκόσμιος Οργανισμός Υγείας (WHO) και η Ευρωπαϊκή Ένωση μείωσαν το μέγιστο επίπεδο ρύπανσης για το αρσενικό (MCL) στο πόσιμο νερό στα 10µg/L. Η εργασία αυτή στόχο έχει να παρουσιάσει το γεωθερμικό πεδίο στην περιοχή της Τρίγλιας (Δυτική Χαλκιδική-Ελλάδα), τη γεωχημεία της περιοχής, καθώς και την αποτελεσματικότητα της τεχνολογίας του στοιχειακού σιδήρου στην απομάκρυνση του αρσενικού από τα γεωθερμικά νερά της Τρίγλιας. Η τεχνολογία αυτή μπορεί να απομακρύνει το αρσενικό σε επίπεδα χαμηλότερα από το MCL.

## **1. INTRODUCTION**

Arsenic contamination in groundwater has gained great attention in recent years because of its toxicity to humans. Arsenic is a toxic metalloid that causes cancer [1]. Its toxicity to humans depends on its concentration and the time of exposure. The World Health Organization (WHO), the US Environmental Protection Agency (USEPA) and the European Commission, in order to minimize the health effects of arsenic, have proposed a new guideline for arsenic ( $10 \mu\text{g/L}$ ). Typical arsenic concentrations in natural waters range from less than  $0.5 \mu\text{g/L}$  to more than  $5000 \mu\text{g/L}$  [2]. High levels of arsenic have been reported in many regions all over the world such as in Argentina, Chile, Mexico, China, Hungary, Bangladesh, West Bengal (India), Vietnam, U.S.A. and Macedonia (Greece).

Arsenic occurrence in ground waters can be attributed to natural and anthropogenic sources. In Greece high levels of natural occurring arsenic are found in different environmental regions. These include: delta sediments, volcanic deposits, geothermal fields, neotectonic active fault areas [3-6]. In addition, arsenic is released to ground water due to anthropogenic causes such as agricultural activities, mining, application of industrial products and industrial waste disposal [2, 7].

Geothermal fields can be found in several volcanic islands (Milos, Santorini, Nisyros etc) and in Mainland Greece along the Hellenic Volcanic Arc (HVA) in South Aegean. The HVA extends over a 450 km length from Korinthos in mainland Greece to the island of Kos in the east [8]. In addition, geothermal fields are located in the areas of Aghia Paraskevi field in Kassandra Peninsula, Petralona-Triglia field in West Chalkidiki, Loutraki field in Aridea province, Lagadas and Nymhopetra- Apollonia fields in the Mygdonia basin, Therma and Sidirokastro fields in Serres Prefecture [9]. Geothermal fields in the Thrace Region are located in Alexandroupolis and Sappes in the area of Mitrikou Lake (Rhodope Prefecture) as well as in Kessani, N. Erasmio, and the Eratino area of Xanthi Prefecture. In this study, we focused on the Triglia-Petalona geothermal field. Triglia is a town in Western Chalkidiki (Central Macedonia).

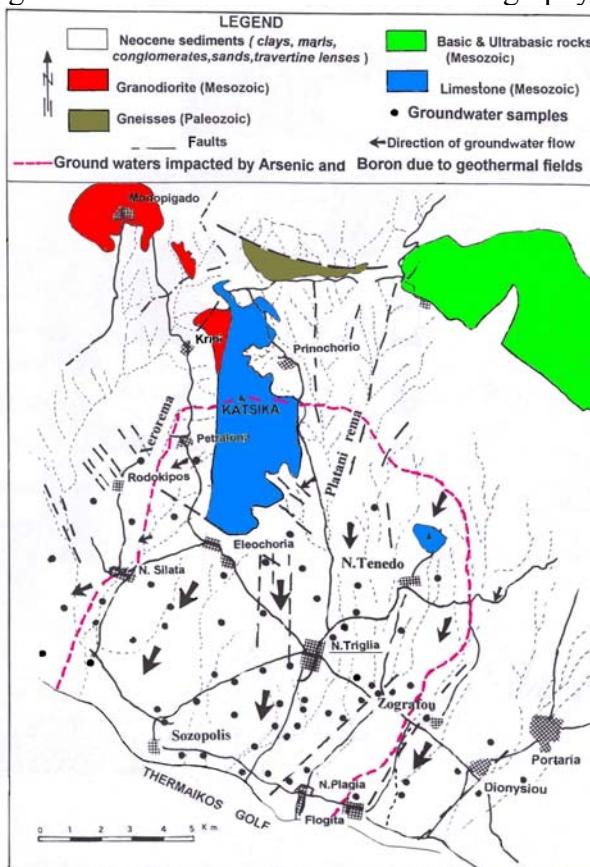
Several arsenic removal technologies have been applied for reducing arsenic in water. Most of the arsenic removal technologies usually include a pre oxidation step for oxidizing As(III) to As(V) in order to improve their performances. Arsenic removal technologies include coagulation-precipitation, ion exchange, adsorption with activated carbon, activated alumina, iron-oxide-coated materials and membrane separation. A new technology (The Arsenic Remediation Technology, AsRT) has been developed for arsenic removal from aqueous solutions at the University of Connecticut [10]. This technology uses zero-valent iron for removing arsenic and it does not require a pre-oxidation step.

The objective of this paper is to present the geothermal field in the region of Triglia Petralona (West Chalkidiki), the geochemistry of this region and also the effectiveness of AsRT in treating a water supply well in Triglia.

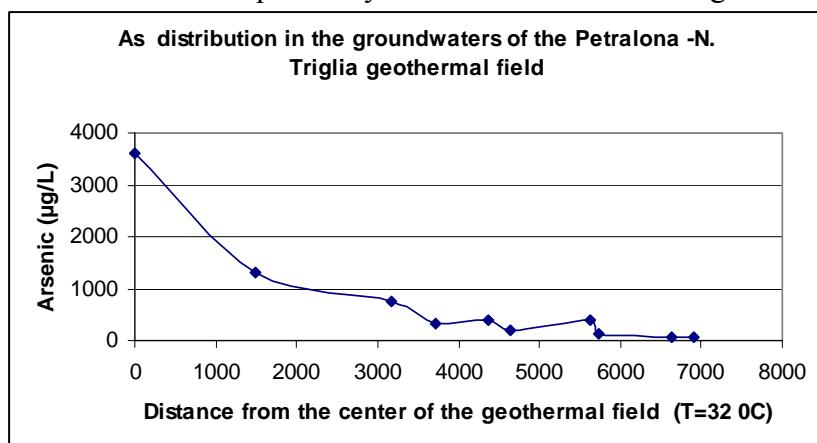
## **2. STUDY AREA**

Arsenic contamination in Triglia is caused by the Katsika karstic geothermal water ( $29-41^{\circ}\text{C}$ ), where the concentration of arsenic varies from 1000 to 2000  $\mu\text{g/L}$ . The warm water percolates into the surrounding Neogene sediments and through the mixing process contaminates the ground waters in the coastal plains porous sediments. In Triglia (3000 inhabitants) and Plagia (1200 inhabitants) the average water consumption for drinking purposes is  $1000 \text{ m}^3/\text{day}$ , but during the summer the population in Plagia increases to 15000 inhabitants and the drinking water consumption is about

4500 m<sup>3</sup>/day. Due to arsenic contamination (40-160 µg/L) two potable water wells in Triglia and three potable water wells in Plagia were abandoned. Furthermore the arsenic concentration in the irrigation wells located in the unconfined aquifer ranges from 60 to 700 µg/L. Unfortunately most of the potable water wells in Triglia have arsenic concentrations above the drinking water standards (10 µg/L) [9]. Geothermal waters are associated with high arsenic concentration in many parts of the world [2]. Figure 1 shows the area where groundwaters are impacted by arsenic (>20 µg/L) and boron (>1000 µg/L) due to the geothermal fields of Katsika mountain. In geothermal water the arsenic content varies from 1000-3000 µg/L and after mixing with cold waters of the porous aquifers, the arsenic content decreases gradually. In the coastal area the arsenic varies from 20 to 150 µg/L. The decrease in arsenic concentration is not always linear because it depends on the depth of the well, the seepage of the surficial waters and the stratigraphy of the region (Figure 2).



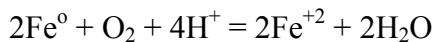
**Figure 1:** Ground waters impacted by arsenic and boron due to geothermal fields.



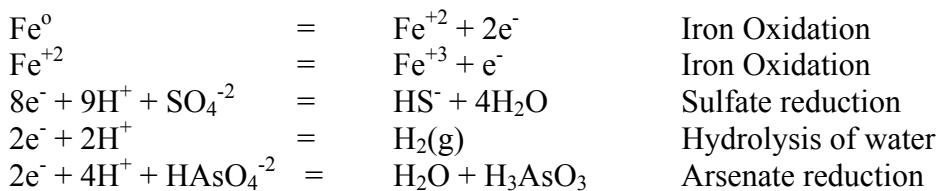
**Figure 2:** Distribution of arsenic in the groundwaters of the Petralona-N Triglia geothermal field

### 3. DESCRIPTION OF AsRT

AsRT technology uses iron filings (zero-valent iron) and sand to reduce inorganic arsenic species to iron co-precipitates, mixed precipitates, and in conjunction with sulfates to arsenopyrites [10]. The immobilization of arsenic is accomplished by passing inorganic arsenic contaminated water through an iron filings/sand (1:1 by weight) "filter" (arsenic removal reactor). The chemical processes that take place in the filter are: Elemental iron ( $\text{Fe}^0$ ) is oxidized to ferrous iron ( $\text{Fe}(\text{II})$ ). The oxygen present in the solution (aerobic conditions), will be consumed according to the reaction:



This reaction will utilize all oxygen, and it will cause a temporal decrease in the pH of the solution. When the solution becomes anaerobic, iron oxidation will be coupled with the hydrolysis of the water, sulfate reduction, and arsenate reduction as follows:



The above reactions form precipitates that include  $\text{Fe(OH)}_3$ ,  $\text{FeAsO}_4$ ,  $\text{FeAsS}$  and others. Inorganic arsenic species could also be removed from the solution through the formation of co-precipitates, mixed precipitates and by adsorbing onto the ferric hydroxide solids.

An iron removal reactor follows the arsenic removal reactor. The iron removal reactor consists of an aeration unit and a filtration unit. In the aeration unit ferrous iron ( $\text{Fe}(\text{II})$ ) is oxidized to ferric iron ( $\text{Fe}(\text{III})$ ) and ferric hydroxide ( $\text{Fe(OH)}_3$ ) is formed. The aeration unit is followed by an iron filtration unit. The remediation process can be enhanced by passing the arsenic contaminated water, over a sulfate source (barite) or by introducing sulfate ions in the solution. The presence of the sulfate ions provides the opportunity of arsenopyrites precipitation.

Previous studies [11] suggest that the mechanism of arsenic removal from zero valent iron is a combination of abiotic surface precipitation and adsorption. The precipitant formed is highly related to sulfur content at the surface of iron filings. In addition, the technology can remove effectively both As(III) and As(V), without the use of a pre-oxidation step. Arsenic removal by zero valent iron is related to surface area and type of iron filings, the rate of iron corrosion, pH and redox conditions. The AsRT technology has been tested successfully in many parts of the world including Maine (U.S.), New Jersey (U.S.), Bangladesh, Chalastra (Central Macedonia, Greece), and in this case in Triglia (West Chalkidiki, Greece) [9,11,12].

### 4. AsRT PILOT TEST IN TRIGLIA

An AsRT pilot system was tested in a well in Triglia during the month of September, 2002 (30 days of operation). The system consisted of an arsenic removal reactor followed by an iron removal unit. The iron removal reactor had an aeration unit and a 0,05 micron filter filtration unit. The arsenic removal reactor consisted of two columns in series filled with sand and iron filings (1:1 by volume). The total Bed Volume of the arsenic removal reactor was 5,4L. The mean flow rate of water was 9.5 L/hr or (1.76 BV/hr) during the first 2 days and 6L/hr (or 1,11BV/hr) during the remaining time of operation. In the field arsenic was measured with a Hach 2000 spectrophotometer using the Mo-

blue method. Arsenic speciation analysis was accomplished with disposable cartridges [13]. In the field pH was measured with an ORION pH combination electrode while Eh was measured using an ORION ORP electrode. From the first day of operation the corrosive power of the water was sufficient to cause iron corrosion and arsenic removal. All experiments were conducted in ambient pH, and all the parameters remained unaltered in order to evaluate the AsRT technology operation under field conditions. During the arsenic removal process the DO was reduced due to the reaction of oxygen with zero valent iron. The pH increased in the system while the redox potential decreased as expected. In the first day the concentration of total arsenic decreased from 137 µg/L to 7 µg/L. Table 2 presents the average inflow and outflow water quality for days 20 and 27 of operation. All parameters presented in Table 2 were analyzed in the lab. Arsenic was determined by hydride generation-flame atomic adsorption spectrometry using a PERKIN ELMER M2100 atomic adsorption spectrophotometer. All ions were analyzed using a METROHM Ion Chromatograph. The influent groundwater had similar water quality parameters during the experiment. Arsenic speciation results revealed that the influent at the 27<sup>th</sup> day contained 4.44% As(III) and 95.6% As(V).

The concentration of arsenic in the effluent was below the drinking water standards (<10 µg/L). Speciation in the effluent could not be conducted due to low arsenic content. As expected phosphate concentration decreased during the process because phosphate ions are well known inner-sphere complex forming anions that can be adsorbed to iron oxide surfaces or can precipitate to form discrete solid phases on mineral surfaces [13].

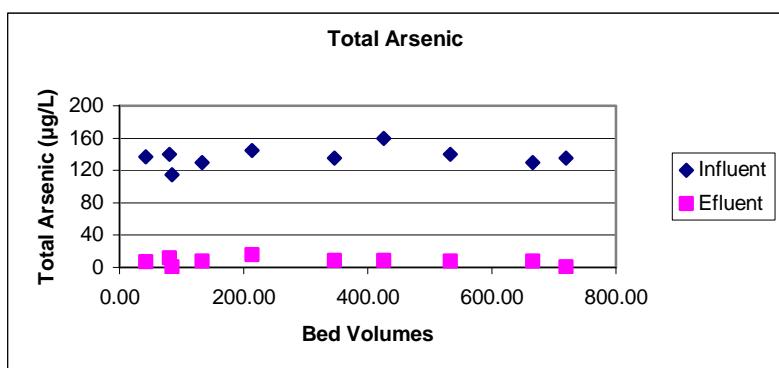
**TABLE 2: Average Water Quality**

Parameter	Influent (23/9/2002)	Effluent (23/9/2002)	Influent (30/9/2002)	Effluent (30/9/2002)
pH	6,94	7,29	7,05	7,25
Conductivity (µS/cm)	1386	1330	1359	1220
Ca <sup>2+</sup> (mg/L)	108,21	93,78	105,81	93,30
Mg <sup>2+</sup> (mg/L)	81,50	79,01	83,44	86,34
Na <sup>+</sup> (mg/L)	100,0	110,0	100,0	100,0
K <sup>+</sup> (mg/L)	7,0	6,0	7,0	6,0
NH <sub>4</sub> <sup>+</sup> (mg/L)	0,026	-	0,110	4,370
HCO <sub>3</sub> <sup>-</sup> (mg/L)	634,4	622,2	627,0	536,8
Cl <sup>-</sup> (mg/L)	163,1	173,7	159,6	173,7
SO <sub>4</sub> <sup>2-</sup> (mg/L)	42,6	41,3	44,0	40,3
NO <sub>3</sub> <sup>-</sup> (mg/L)	43,8	40,0	42,8	9,8
NO <sub>2</sub> <sup>-</sup> (mg/L)	<0,001	-	<0,001	0,425
PO <sub>4</sub> <sup>3-</sup> (mg/L)	0,478	0,045	0,600	0,165
B(mg/L)	1,8	1,6	1,7	1,6
F(mg/L)	0,25	0,36	0,42	0,66
SiO <sub>2</sub> (mg/L)	24,3	11,0	27,7	11,0
Fe (mg/L)	0,04	0,018	<0,001	0,002
Mn (mg/L)	<0,001	0,130	0,032	0,091
As (Total) (µg/L)	140	8	135	<1
As(V) (µg/L)			129	
As(III) (µg/L)			6	

- Lab accident

The results obtained from Table 2 revealed a remarkable increase in  $\text{NH}_4^+$  concentration while  $\text{NO}_3^-$  concentration decreased during the experiment. More specifically, the concentration of ammonia and nitrite increased by 242,8 mmol/L and 9,22  $\mu\text{mol}/\text{L}$  respectively while the concentration of nitrate decreased by 532,26  $\mu\text{mol}/\text{L}$  during the sampling period of 30/9/2002. In addition the concentration of nitrate decreased by 61,26  $\mu\text{mol}/\text{L}$  during the sampling period of 23/9/2002. The fact that more nitrate was reduced between the first and the second sampling period can be easily explained by the increase in the rate of corrosion of iron filings as the times progresses [11]. These results can be explained by the reduction of nitrate by iron filings. Since nitrate reduction was higher than nitrite and ammonia generation, we postulate that a portion of nitrate was denitrified to produce nitrogen gas while the rest was converted to nitrite and ammonia. More studies need to be conducted to elucidate this mechanism, since high ammonia concentrations is a water quality problem.

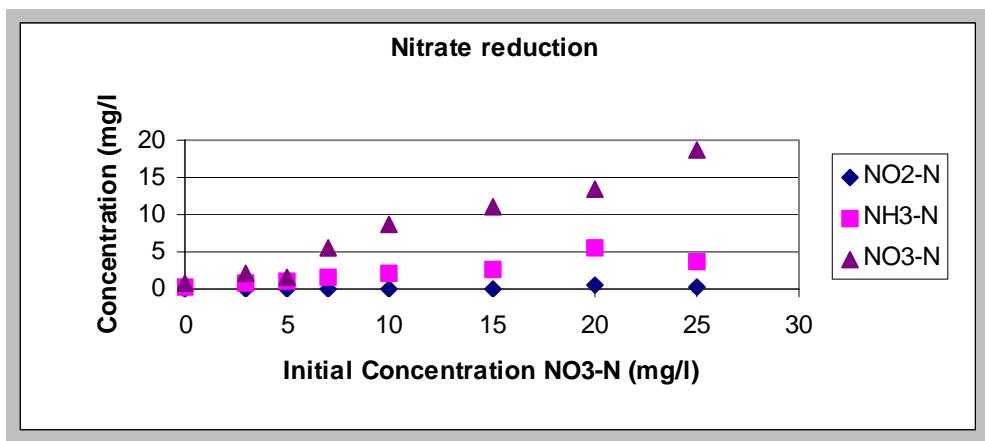
Figure 3 presents the influent and effluent concentration of arsenic versus bed volumes during the experiment. The inflow arsenic concentration ranged from 115  $\mu\text{g}/\text{L}$  to 160  $\mu\text{g}/\text{L}$  while the effluent arsenic concentration ranged from 1  $\mu\text{g}/\text{L}$  to 16  $\mu\text{g}/\text{L}$ . The average effluent arsenic concentration was 7.9  $\mu\text{g}/\text{L}$ , which is below the drinking water standards.



**Figure 3:** Influent and effluent arsenic concentrations

## 5. LABORATORY BATCH EXPERIMENTS

In order to evaluate nitrate reduction and ammonia formation by iron filings, laboratory batch experiments were conducted. 2 gr of iron filings were mixed with 200 mL of aqueous solution, containing a known concentration of nitrates and an initial arsenic concentration of 8000  $\mu\text{g}/\text{L}$ , and were placed in polyethylene bottles. Each bottle had different concentration of nitrates in the range of 0 to 25 mg/L. The initial pH of the solution was adjusted to 6.9 in order to accomplish field pH conditions in Triglia. The bottles were then placed on a rotary shaker at room temperature for 5 days (equilibrium time). After five days the supernatant was filtered through a nylon filter 0,2 $\mu\text{m}$  and analyzed for nitrates, ammonia and nitrite ions. Figure 4 presents the concentration of nitrate, ammonia and nitrite ions versus the initial nitrate concentration. The experimental results indicate that the initial concentration of nitrates was converted mostly to ammonia. The percentage of conversion was 20 %.



**Figure 4.** Nitrate reduction –Formation of ammonia

## 6. CONCLUSIONS

Field and laboratory experiments suggested that the AsRT technology can effectively reduce arsenic concentration from groundwater in geothermal regions. In addition, it was shown that the technology can be used to treat water in regions where nitrate and arsenic contamination is reported, for example agriculture regions. The only drawback is the formation of ammonia. Therefore continuous monitoring of ammonia concentration is required. If the concentration of ammonia exceeds the proposed limits an ammonia removal unit must follow AsRT technology.

## ACKNOWLEDGEMENTS

This project was funded by the General Secretariat for Research and Technology, Hellenic Ministry of Development as part of a Greek-Hungarian Collaboration. We would like to thank the Hungarian research team Dr. Jozsef Hlavay and Dr. Klara Polyak, University of Veszprem for an excellent collaboration.

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