IN-SITU REMOVAL OF ARSENIC FROM GROUNDWATER USING PERMEABLE REACTIVE BARRIERS WITH IRON BASED SORBENTS

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Abstract

Four types of materials have been used in the construction of permeable reactive barriers (PRB) used in the treatment of arsenic contaminated groundwater: zero valent iron (ZVI), furnace slag, sorbents and composite materials (organic + ZVI or a sorbent). Although barriers using sorbents are promising they are the less studied and no real applications, to our knowledge, have been implemented to the present. There are no published systematic studies regarding the potentialities of some iron oxides and hydroxides that are available in the market for a long time, such as ARM 300 and GEH 102.

This research analyzes the capacities and drawbacks of these last two sorbents as materials for in-situ removal of arsenic using laboratory studies at batch scale and continuous operation in columns. Isotherms and breakthrough curves were determined for different operating conditions that are compared. Both sorbents adsorb As(III), As(V) and mixtures of both. Breakthrough curves allow determining the uptake capacity of both sorbents that are similar, 20 g As/ kg, a consistent value somehow inferior to values already published in the literature.

Finally it is studied the spatial distribution of arsenic concentration in the sorbent particles using an electron probe microanalyzer (EPMA) to produce backscattered electron images (BSE) and elemental mapping through wavelength-dispersive spectroscopy (WDS). Results show that sorbent particles adsorb arsenic through chemisorptions: arsenic enrichment coincides with depletion in oxygen and iron. Spatial mapping of the concentrations allows infer that the removal mechanisms are different: while for ARM 300 reductive precipitation is relevant for GEH 102 the adsorption mechanisms with complex formation are prevalent.

Keywords: iron based sorbents, in-situ arsenic removal, permeable reactive barriers, breakthrough curves.

1. Introduction

Anomaly arsenic concentrations in groundwater are generally of natural origin and caused by natural dissolution of minerals. Arsenic is always present in natural waters either in the reduced form As(III) or in the oxidized form As(V). Toxicity depends upon the chemical specie and, in general, As(III) is 25 to 60 times more toxic than As(V). Arsenic concentrations in clean superficial waters and in groundwater are normally in the range $1 - 10$ µg/L. Very high concentrations in As (> 1000 µg/L) have been found in different areas like Taiwan, West Bengal, India, Bangladesh, Mexico and some areas in Argentina, Chile and the United States. Arsenic is also a problem in many countries of the European Community. For instance in the Great Hungarian Plane and some areas in Romania concentrations between 150 and 180 µg/L are found. In Portugal and Spain it is possible to find concentrations of As in former mining areas ranging from 100 to 2000 ppb.

Conventional technologies for the treatment of groundwater like pump and treat have important disadvantages: very high costs, especially if the treatment is long, and a general reduced efficiency. For this reason the in-situ technologies have received greater attention in the last years. Some alternatives are available like bioremediation, permeable reactive barriers, in-situ chemical treatment, enhanced natural attenuation and electro-kinetics. Permeable reactive barriers is the in-situ technology that has received more attention and some applications were built in several countries.

Several materials have been tested and used for the in-situ treatment of arsenic contaminated groundwater. We briefly refer those with more application: a) zero valent iron (ZVI); (b) furnace slag produced in iron works; c) sorbent materials such as iron hydroxides and activated alumina and d) multifunctional barriers, either multiple or composite, constituted by a first barrier with compost or other organic material that promotes the microbial reduction of sulphates followed by a second layer (or barrier) constituted by ZVI or other sorbent.

In the barriers that use granular ZVI Fe is oxidized and FeOOH is produced at the surface of the grains; this compound has capacity to adsorb metals and metalloids such as arsenic (Nikolaidis, 2003). ZVI is a very efficient reducing agent that can remove both inorganic and organic arsenic. The kinetics is very fast; for instance McRae (1999) observed the removal of As(V) from concentrations of 1000 to <3 μg L^{-1} in two hours. Kinetics is also fast with mixtures of As(III) and As(V). Mineralogical studies show that As(V) is reduced and co-precipitates with Fe that remains as goethite at the surface of the ZVI particles. Bang et al (2005) refers that As removal is dramatically affected by the dissolved oxygen and the pH of the solution.

In July 2005 a pilot-scale permeable barrier was constructed near Helena, Montana (USA), with a depth of 14m, 9.1 m long and 1.8 to 2.4 m wide (in the direction of groundwater flow). The barrier was located near an ancient lead foundry and was designed to treat moderate concentrations both in As(III) and As(V). After two years of operation, the concentrations downstream the barrier were significantly lower as mentioned by Wilkin (2008) and Beak & Wilkin (2009).

Baker (1998) used as a reactive medium a slag constituted by a mixture of iron oxides, calcium oxides and limestone. The tests showed the capacity for removal of not only As(III) and As(V), but also mixtures of both species, from 1000 to less than 3 μg L^{-1}. This solution was implemented at a real scale at the "Dupont Site", built east of Chicago, using *Basic Oxygen Furnace Slag* (BOFS) for the remediation of the groundwater contaminated with arsenic. The slag is rich in iron and in calcium oxi-hydroxides. The reactive medium oxidizes As(III) to As(V) that is sequentially adsorbed at the slag surface. pH increases and may reach values as high as 12. The system comprises two reactive barriers at a distance of 5m apart. McRae (1999) tested materials that could be used for removal of As(III) and As(V) in PRB mixtures between BOFS (*Basic Oxygen Furnace Slag*) and activated alumina (AA). The mixture that was tested had 10% slag and 20% activated alumina inserted in a mixture of limestone and silica sand. In this case, the mechanism of attenuation is sorption. Nevertheless the usage of slag without other components evidenced poor results and cannot be considered as a feasible option.

Granular Ferric Hydroxide (GFH) and Granular Ferric Oxide (GFO) are excellent arsenic sorbents. GFH are prepared from a ferric chloride solution that precipitates with sodium hydroxide; particles are then washed, centrifuged and grained under pressure (Driedhaus *et al*, 1998). Aqueous silica reduces the GFH capacity for the removal of As(V).

Some of the Iron Based Sorbents (IBS) available in the market are the following: Adsorpas (Technical University of Berlin), ARM 300 (BASF), G2 (ADI International), SMI III (SMI), GEH 102 (GEH Wasserchemie GmbH & Co. KG) and Bayoxide E33 (Bayer AG). Sorption is of chemical origin and thus irreversible. These materials can be used either in fixed bed columns, similar to those used with Activated alumina (AA) or in PRB. In this study we tested ARM 300 that is an iron oxide (Hematite, α-Fe$_2$O$_3$) and GEH 102 that is a granular iron hydroxide (Fe(OH)$_3$ and FeOOH Akageneite (β-FeOOH)).

Ipsen (2005) in a research concerning the identification and testing of materials that could be used in PRB refers that the sorbents that evidenced better behaviour were materials based in akaganeite/ferrihidrite (β-FeOOH/Fe$_2$O$_3$.5H$_2$O). The commercial product GEH had a loading capacity of 36 g As/kg exhibiting the best behaviour between all the tested materials. Minerals of the goethite type (α-FeOOH) improved with additions of titanium exhibit lower loading capacities. The authors of this article, Silva et al (2009), as part of this research project, also tested other sorbent materials such as hydrous ferric oxide (HFO) and hydrous ferric oxide loaded into activated carbon (HFO/AC); nevertheless, their loading capacity was lower.

The fourth type of conception for PRB is the composite barrier or the multiple functional barrier. They are based in the following principles: the first barrier where the reactive material is organic matter, generally compost or wood chips, promotes the biologic mediated reduction of the sulphates with subsequent precipitation of metallic sulphides.

This barrier is located upstream relatively to the source of arsenic contamination. A second barrier is built downstream using ZVI. The following reactions occur: the sulphides liberated by the organic matter may promote and initiate the reductive dissolution of the arsenic loaded in Fe and Mn oxides and hydroxides; this originates an increase in the As concentrations during a short time of the arsenic elution and reduces the time needed for rehabilitation; on the other hand, the precipitation of sulphides reduces the As emissions increasing the life time of the downstream barrier; precipitations occur as As_2S_3 or by co-precipitation with iron sulfides; if the concentration of sulphates in water are too low they can be increased by the addiction of gypsum. Several researchers studied this potential type of PRB, such as Köber (2005) and Gibert (2004).

A systematic review analysing the in-situ technologies for arsenic removal is presented by Cortina et al (2010).

3. Materials and methods

All chemicals were reagent grade used without any further purification. All solutions were prepared with deionised water. All glassware was cleaned by soaking in 10% HNO_3 and rinsed with deionised water. Arsenic solutions were prepared by direct dilution of a 1000 mg/L standard solutions from Fluka for As (V) and from Panreac for As(III) and were kept in dark glass flasks for the preparation of all the required diluted solutions.

Total arsenic determinations were carried by inductively coupled plasma optical emission spectroscopy with coupled hydride generation. Arsenic III was determined by catodic stripping voltammetry with square wave using a hanging mercury drop electrode as described by Ferreira and Barros (2002). Samples that were not analysed immediately were preserved by acidification to a pH lower than 2 with concentrated HCl and stored in acid washed high-density polyethylene containers (ISO, 1994). All samples were analysed within seven days after collection. The pH values were obtained by immediate measurement using a pH meter (Crison, GLP22). The sand used was pure quartz that was washed, dried and sieved to grain sizes between 710 e 1000 µm. The commercial sorbent ARM 300 was supplied by BASF and GEH 102 by Wasserchemie GmbH & Co.

Column tests were performed at 20 ºC. The solutions contaminated with As were artificially prepared and they were pumped from a large volume container using a peristaltic multi-channel Ismatec BV-GES pump into an Omnifit column with an internal diameter of 2.5 cm and a total height of 15 cm. Later, larger columns (3.1 cm in diameter and 40 cm in height) were also used. Cumulative effluent volumes were periodically measured and samples were simultaneously collected for chemical analysis.

4. Preliminary tests

The tests were performed using: a) solutions only with As(III); b) solutions only with As(V) and c) solution with both As(III) and As(V). The sorption isotherms were obtained using flasks with 100 mL of a solution with a concentration in As of 5 mg/L and adding different masses of sorbent. Control tests were simultaneously performed in the same way but without sorbent. The flasks were incubated in an orbital shaker (Ritabit, Selecta) during 24 hours. After, the pH was measured and the content was filtered under pressure; a sample of 10 mL was collected from each flask and preserved by adding 100 µL of HCL at 37%. This procedure was used both for As(III) and As(V). Figure 1 shows the isotherms for ARM 300.
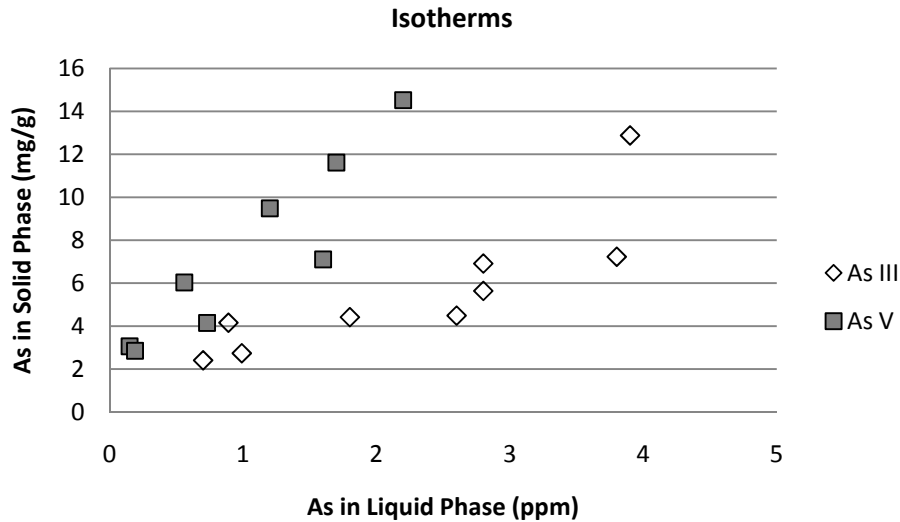
Isotherms

Figure 1 – Sorption isotherms for As(III) and As(V) using ARM 300

The isotherms suggest that As(V) is more adsorbed to ARM 300 than As(III). Similar results were obtained for GEH 102.

The continuous tests through a fixed bed sorption column filled with the reactive medium mixed with quartz sand, were programmed in order to quantify the influence of the interstitial water velocity through the pores. Three different flowrates were used – 5, 10 and 20 mL/min corresponding respectively to interstitial velocities of 1.698×10^{-4}, 3.395×10^{-4} and 5.09×10^{-4} m/s. The last value was the highest that could be safely used taking into account the size and the characteristics of the column. The cumulative effluent volume was periodically measured and samples were collected for immediate measurement of pH and conductivity. HCl was then added for preservation until the chemical analysis was performed.

The general conclusions could be drawn from these experiments:
- The pH, starting from neutral water, decreases slightly with time;
- The conductivity decreases from 250 to 186 μS cm^{-1}.
- Hydrogen ions are generated as a consequence of the As sorption by the ARM 300; this proves that the sorption is not only of physical origin but there are also simultaneously chemical reactions involved.

Figures 2 and 3 represent the values for the arsenic concentrations in the effluent normalized by the average initial concentration at the inlet for interstitial velocities for the As(III) and for the velocity of $3.395 \cdot 10^{-4}$ m/s for the As(V).
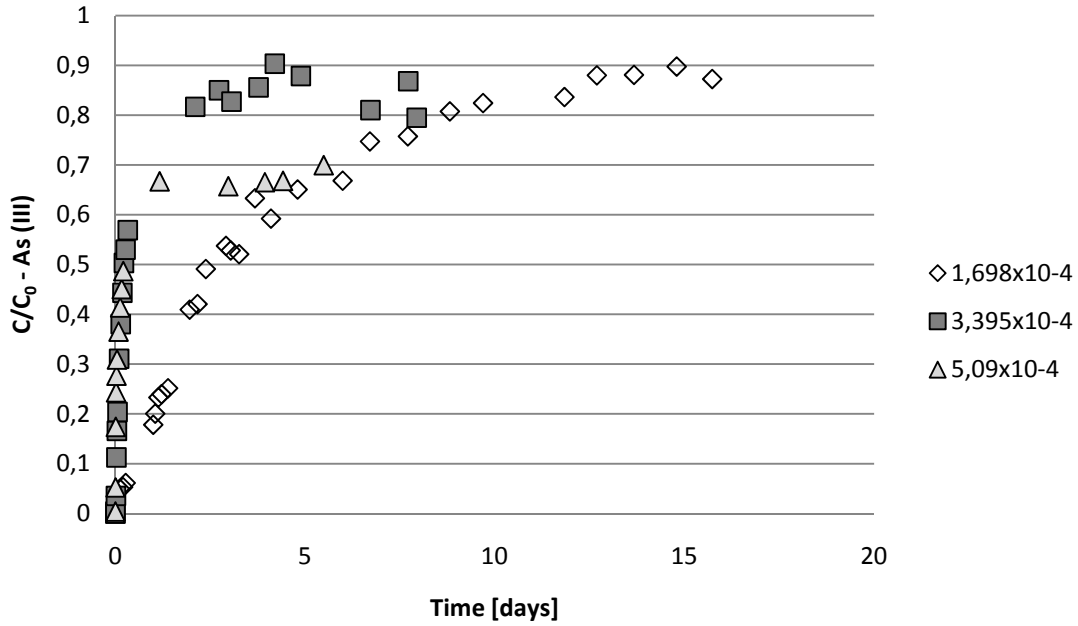
Figure 2 – Time evolution of As(III) concentrations using different interstitial velocities
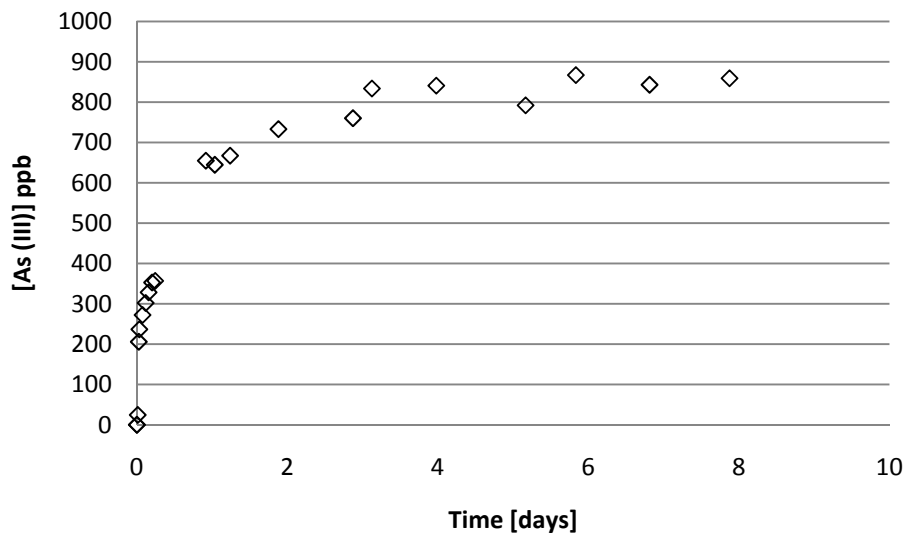

Figure 3 –Time evolution of As(V) concentrations using an interstitial velocity of 3.395.10^{-4} m/s

The average concentration at the inlet (C$_0$) and the experimental breakthrough time corresponding to 50% of the column saturation (t$_{50\%}$) are shown in Table 1 for all the tests. An increase in the interstitial velocity corresponds to a decrease in the t$_{50\%}$. This expected behaviour corresponds to a decrease in the residence time. This relationship is not linear.

Table 1 – Experimental data for the breakthrough time t$_{50\%}$

Arsenic	Flowrate (mL/min)	C$_0$ (μg/L)	t$_{50\%}$ (h)
Arsenic (III)	5	1077	58
	10	1024	46
	20	1109	6
Arsenic (V)	5	984	35
	10	1046	5
	20	1048	4

For the flowrate of 20 mL/min the residence time is much lower than for the other flowrates and leads to a much faster saturation of the column. Comparing both As species for the flowrates of 5 and 10 mL/min it is noticeable that $t_{50\%}$ is higher for As(III), in accordance with the isotherms previously obtained.

The same tests were performed for the same flowrates using a solution with a mixture of As(III) and As(V) in the same proportion. Figure 4 represents $C(t)/C_0$ as a function of the cumulative effluent volume. It is also noticeable that the lowest flowrate allowed a higher proximity to the saturation than the other flowrates tested.
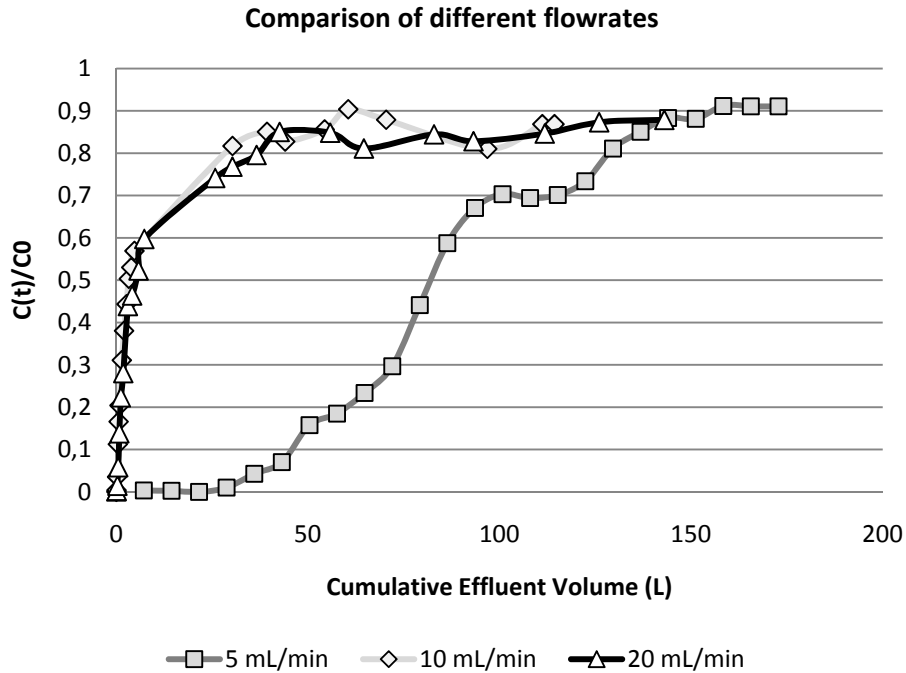
Comparison of different flowrates

Figure 4 – Total arsenic breakthrough curves for different flowrates

The uptake capacities for the flowrates of 5 and 10 mL/min are similar with a value of 20 g As/kg of sorbent.

5. Comparison tests between the sorbents

Comparison tests between ARM 300 and GEH 102 were performed using two columns fed in parallel by the same arsenic solution (around 1000 μg/L) using a multi-channel peristaltic pump. Tests were also performed for each sorbent using the same operating conditions: same amount of sorbent and sand, same concentration in arsenic of the feed solution and same flowrate. These last results are here analyzed.

In both tests 1.5 g of sorbente was used. The sorbents were mixed with pure quartz sand (iron free) and inserted in the column. In the test for the GEH 102, the arsenic feed solution had a concentration of 1136 μg L^{-1} and the average flowrate was 0,115 L h^{-1}, which corresponds to an interstitial velocity of 1.10^{-4} m/s. The flow was ascending and the effluent was collected from the top and periodically sampled. The effluent cumulative volumes were also measured at the same time.

In the test for ARM 300 the feed solution had a concentration of 1002 μg L^{-1} and was fed to the column at an average flowrate of 0,127 L h^{-1} which corresponds to an interstitial velocity of $1.1*10^{-4}$ m/s. The procedures for collecting samples and measuring the cumulative effluent volumes were similar.

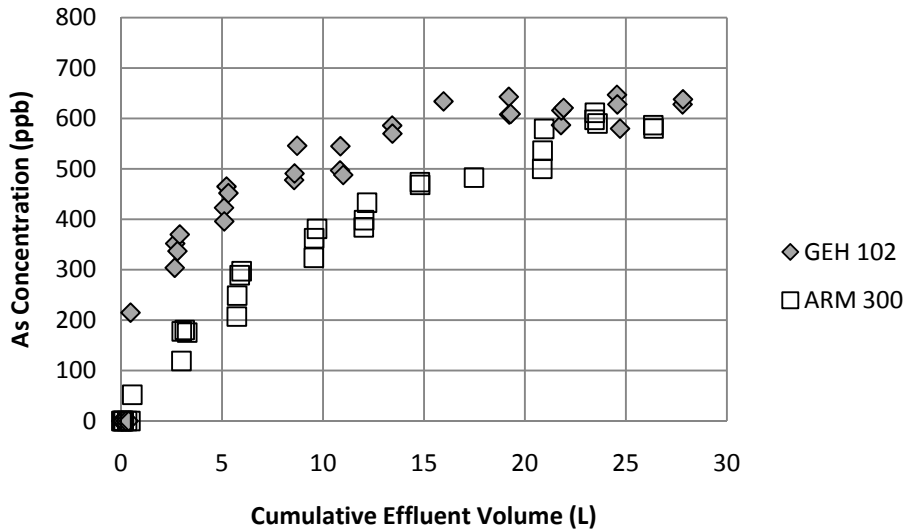The cumulative effluent concentrations for both sorbents are shown in figure 5

Figure 5 – Comparison between ARM 300 and GEH 102

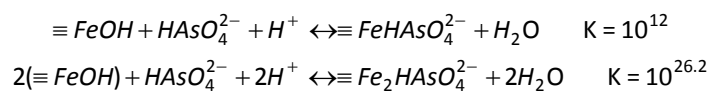The most relevant conclusions are the following:

- The residence time was too short in relation to the kinetics demand. For these reason not all the As had contact time sufficient to be adsorbed;
- This result was not expected because the water velocity recommended for operation with ARM 300 in water treatment columns is $1.3.10^{-3}$ m/s and the velocity used was inferior;
- In both cases the saturation of the uptake capacity was not reached and the volume of water that passed through the column was insufficient;
- GEH 102 demonstrates a slightly better performance;
- An extrapolation method was developed to estimate the uptake capacities of both sorbents and the following results were obtained: 20,6 g of As/kg sorbent for GEH 102 and 20,8 for ARM 300. In a previous study Ipsen (2005) found an uptake capacity of 36 g As/kg for the GEH sorbent.
- In a potential field application it would be required to build two permeable reactive columns, with a reasonable distance between them, so that the second barrier would allow attain environmentally acceptable arsenic concentrations.
- Alternatively, an excess of at least 100% of the sorbent in relation to the necessities estimated by the uptake capacity would be required.

6. Possible removal mechanisms

Several removal mechanisms are possible, such as reductive precipitation of As, adsorption to the iron hydroxides and still mineral formation (Farrell, 2001). The reductive precipitation occurs according to

$$HAsO_4^{2-} + 7H^+ + 5e^- \rightarrow As + 4H_2O \quad E_H^0 = 0.499\,mV$$
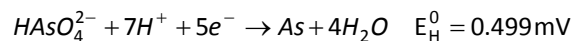
This reaction is very probable with ZVI. Another possibility is adsorption that may occur according with the following reactions (Farrell, 2001)

$$\equiv FeOH + HAsO_4^{2-} + H^+ \leftrightarrow \equiv FeHAsO_4^{2-} + H_2O \quad K = 10^{12}$$

$$2(\equiv FeOH) + HAsO_4^{2-} + 2H^+ \leftrightarrow \equiv Fe_2HAsO_4^{2-} + 2H_2O \quad K = 10^{26.2}$$

In fact both species, As +3 and +5, are removed by mono and bi-dentate complex formation with ferric hydroxides.

Still, another possibility for GEH 102 is the arsenic precipitation according to (Farrell, 2001)

$$Fe(OH)_3 + H_2AsO_4^- + H^+ \rightarrow FeAsO_4 \cdot 2H_2O + H_2O$$
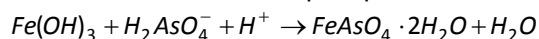
6. Study of the sorption mechanisms using an Electron Microprobe Analyser

In order to enlighten the mechanisms of sorption, samples of the sorbent were collected after their usage in fixed bed columns tests and were analysed using an Electron Microprobe Analyser. The samples were impregnated in resin and polished with diamond paste for examination and analysis by a Field Emission Electron Microprobe (EPMA), model Jeol JXA-8500F. Afterwards, they were coated with carbon to ensure electrical conductivity at the surface. Electron backscattered images were obtained from the sorbent particles. Quantitative analysis at selected points and all WDS X-ray intensity dot maps were obtained with the following operating conditions: 15kV, 60nA and 1µm beam diameter. A dwell time of 10ms was used for X-Ray dot maps.

6.1. Sorbent ARM 300

Figure 6 shows a mapping of arsenic, nickel, oxygen and iron concentrations in a particle of ARM 300 after being submitted to arsenic removal.
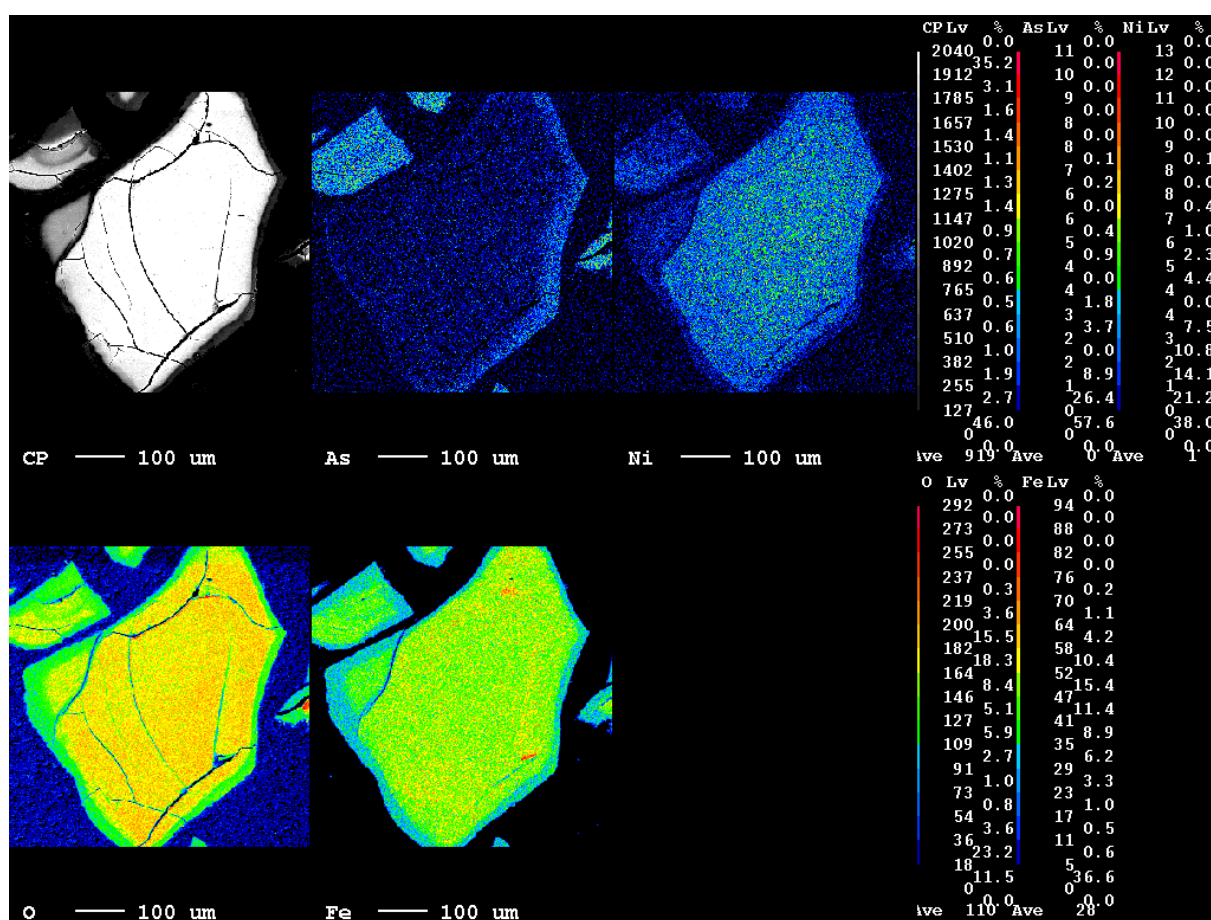
Figure 6 – Mapping of concentration of different elements in a Particle of ARM 300

The observation of the largest particle allows several conclusions:
- The deposition of arsenic was predominantly done at the lower face of the particle, showing that is a superficial reaction; arsenic was not captured at the higher face probably due to the fact that this particle was in contact with another particle of sorbent or sand. Although the sorbent particle has several fractures arsenic has not penetrated to the inner part of the particle through those factures. It can be concluded that it is required for the occurrence of the reaction the existence of an exposed surface in contact with the solution;
- There is a depletion of oxygen concentrations at the surface of the particle independently from the fact whether arsenic was removed or not from that particular surface;
- The same effect happens with iron, although the thickness of the depletion layer is thinner;

- Nickel concentrations are relatively uniform within the particle.
- Due to these changes the sorption is undoubtedly of chemical origin (chemisorption) and thus irreversible.

It should also be noticed as a remarkable fact then existence of a small particle intensely charged in arsenic distributed through all the volume of the particle, at the upper right corner; also a fraction of another particle in the same conditions is seen in the same area. It remains questionable if part of the external adsorbed arsenic layer can be detached from the surface

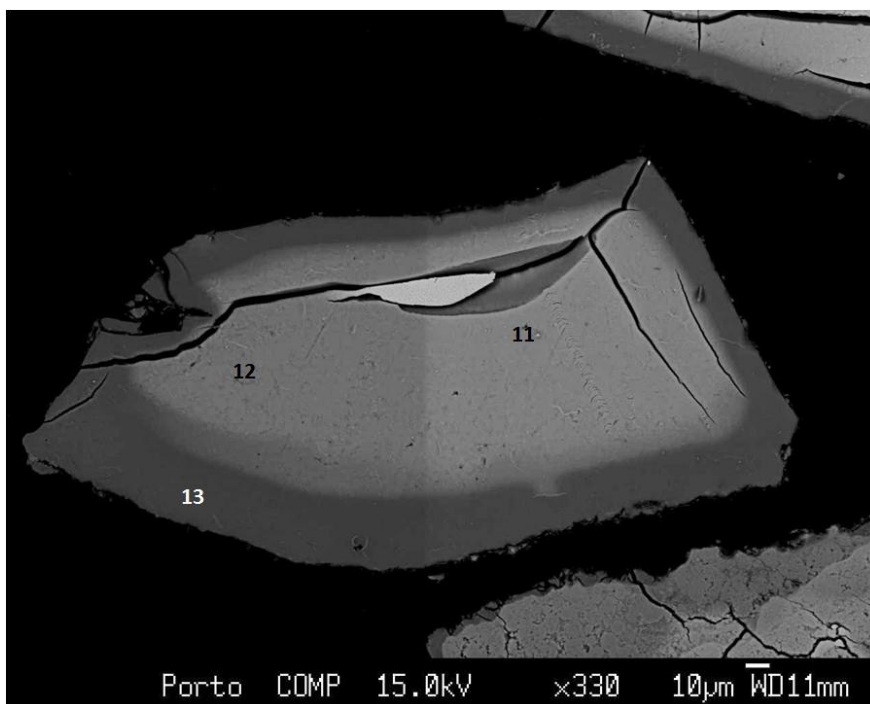Another particle was selected for chemical analysis as shown in Figure 7.

Figure 7 – Points selected for chemical analysis in an ARM 300 particle

Points 11, 12 and 13 were selected for chemical analysis for the following elements Si, Cl, As, Mg, Fe, Cr, S, Al, Mn, Ni, Ti, Zn and Ca. Table 2 shows the results obtained. Concentrations for all the elements are expressed as oxide.

Table 2 – Spatial distribution of concentrations in a particle of ARM 300 (percentage)

Element	11	12	13	Average concentration	Standard deviation
SiO_2	1.3759	1.1374	0.6826	1.065	0.352
Cl	0.6966	0.6976	0.6902	0.695	0.004
As_2O_5	2.82	3.07	3.59	3.160	0.393
MgO	0.0974	0.0964	0.0505	0.081	0.027
FeO	64.51	64.91	54.84	61.420	5.702
Cr_2O_3	0.005	0.0076	0.0541	0.022	0.028
SO_3	0.6799	0.7282	1.1243	0.844	0.244
Al_2O_3	0.2535	0.0919	0.2078	0.184	0.083
MnO	0.2564	0.2846	0.1925	0.245	0.047
NiO	0.794	0.7465	0.0507	0.530	0.416
TiO_2	0.0747	0.0817	0.0209	0.059	0.033
ZnO	0.5027	0.7062	0.0392	0.416	0.342
CaO	0.475	0.5304	0.7395	0.582	0.139

Total	72.5412	73.0886	62.2824			

The concentration of adsorbed Arsenic is higher at the surface of the sorbent although arsenic has apparently penetrated to the inner part of the particle, even if the particle has a large size (scale is indicated at the picture). Nevertheless, concentrations decrease from the outer to the inner side of the particle. Notice that the highest concentration in As coincides with the lowest concentration in Fe suggesting that part of the Fe is reduced to a soluble Fe(II) form. A reductive precipitation is possible and probably coexisting with other removal mechanisms.

6.2. Sorbent GEH 102

Figure 8 shows the mapping of the concentrations for different elements (As, Ni, O and Fe) in a particle of GEH 102 after it was exposed to arsenic sorption in a fixed bed column during 30 days.
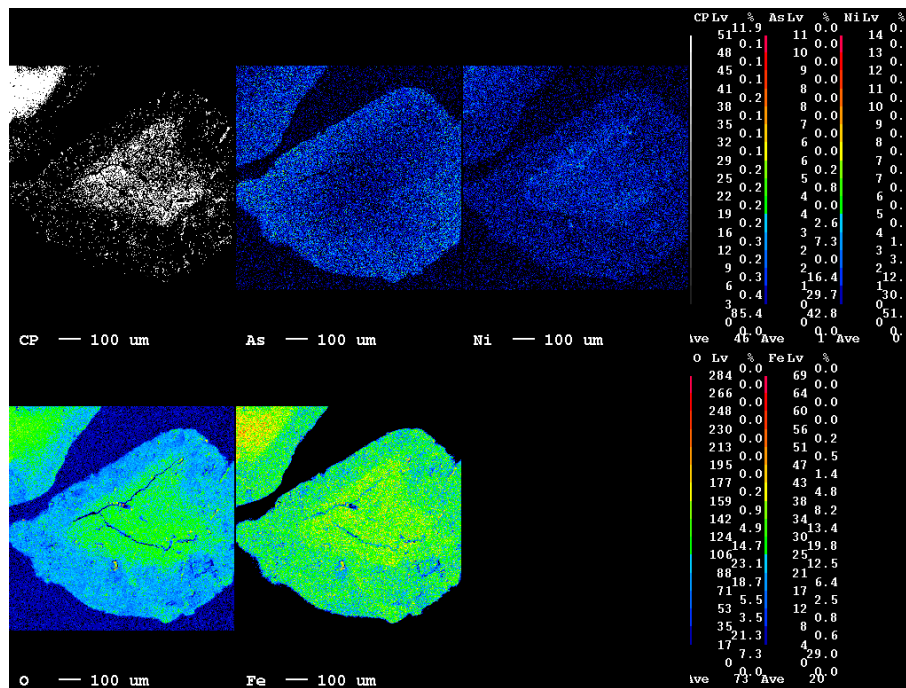

Figure 8 – Mapping of concentrations in a particle of GEH102

The following observations may be noticed:
- Arsenic is captured around all the external surface of the sorbent particle constituting a layer with variable thickness;
- The increase in arsenic concentrations coincide with a net depletion in oxygen;
- Iron concentrations remain approximately constant inside the particle.

Figure 9 presents another set of sorbent particles and the mapping of iron concentrations. It is noticeable a decrease in the concentrations at the outer surface of the particles. Concentrations in the inner part are approximately homogeneous although small heterogeneities with higher concentrations can be noticed.
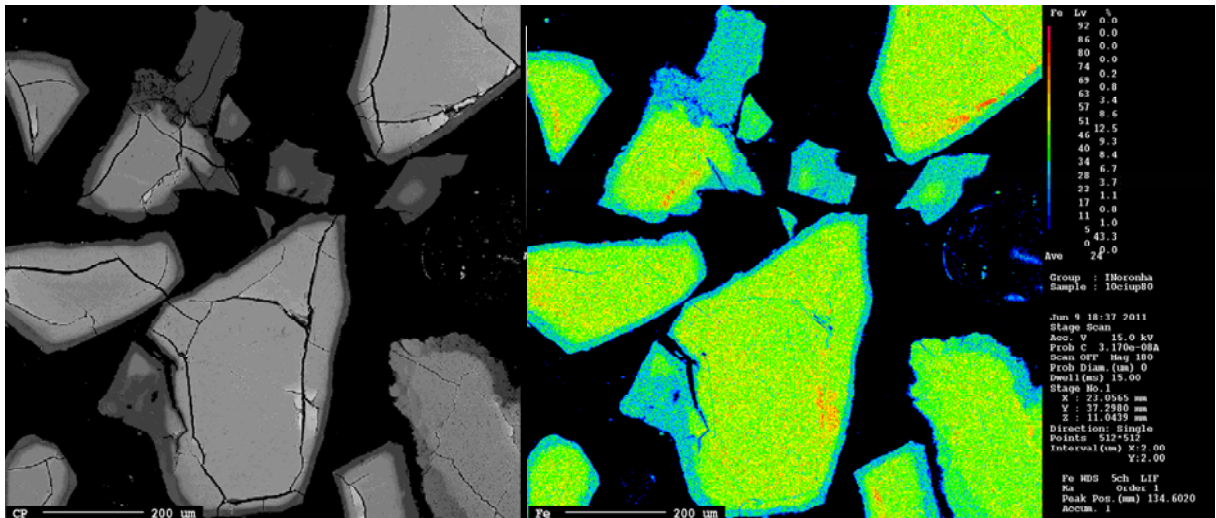
Figure 9 – Iron concentrations in a set of particles

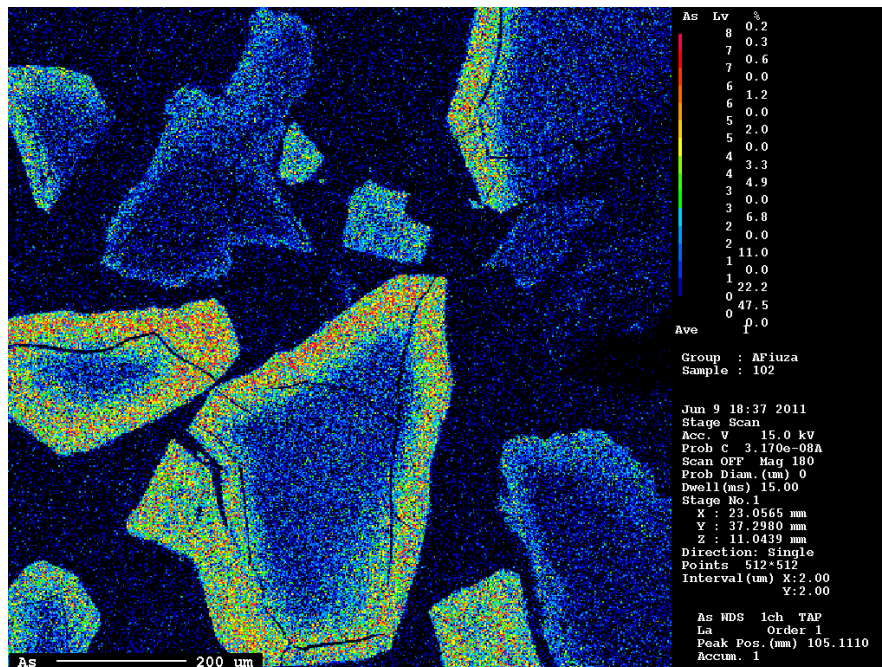The mapping of arsenic concentrations was also performed (Figure 10)

Figure 10 – Mapping of As concentrations

Some facts:
- Arsenic is captured through the exposed surface of the particles. If some particles present only a part of the external surface with higher arsenic concentrations it is due to the fact that the particle was in contact with another (sorbent or sand) and the surface didn't contact the arsenic solution;
- One of the particles didn´t captured arsenic, probably due to the reasons already exposed;
- The thickness of the sorption layer may reach values as high as 40 μm.

One of the particles was selected for quantitative chemical analysis (Figure 11).
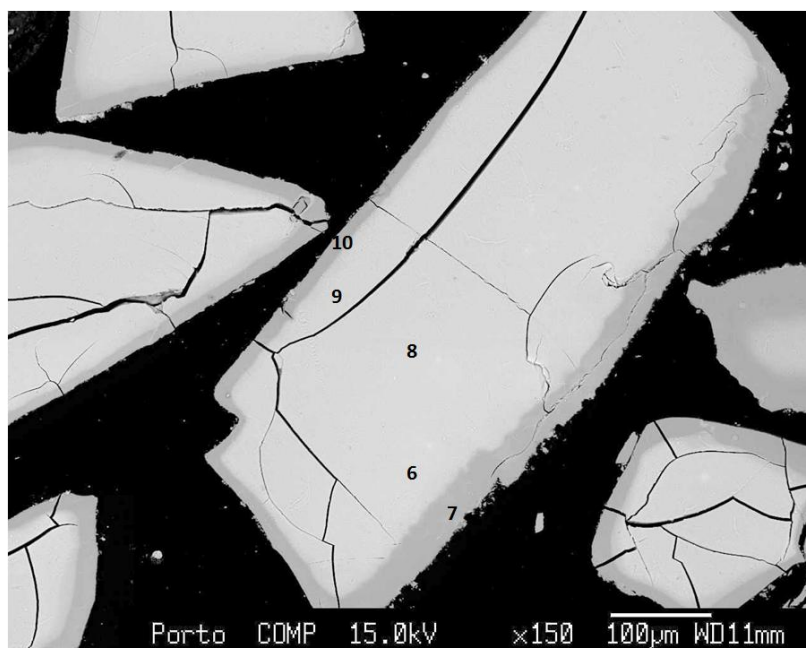
Figure 11 – Selected particle and points that were submitted to chemical analysis

Five points, designated from 6 to 10, were submitted to chemical analysis. Points 7 and 10 correspond to an external layer that was in contact with the contaminated water; points 6 and 9 are inside the particle bur near the external contact layer and point 8 is the core of the particle. Thirteen elements were analysed: Si, Cl, As, Mg, Fe, Cr, S, Al, Mn, Ti, Zn e Ca. Results are presented in Table 3.

Table 3 – Spatial distribution of concentrations in a particle of GEH 102 (Percentage)

Element	6	7	8	9	10	Average concentration	Standard deviation
SiO_2	1.804	0.9861	2.0836	1.5214	0.841	1.447	0.529
Cl	0.6641	0.607	0.6755	0.7179	0.69	0.671	0.041
As_2O_5	1.0785	0.9742	-	1.92	2.47	1.611	0.712
MgO	0.0279	0.1015	-	0.1326	0.0187	0.070	0.056
FeO	64.08	51.01	65.68	67.16	56.78	60.942	6.836
Cr_2O_3	-	0.0351	-	0.0161	-	0.026	0.013
SO_3	0.7387	0.4951	1.024	1.0029	0.6738	0.787	0.225
Al_2O_3	0.1067	0.1179	0.0862	0.1914	0.1233	0.125	0.040
MnO	0.2855	0.0286	0.1215	0.1568	0.2214	0.163	0.098
NiO	1.0415	0.0078	1.0148	0.9871	-	0.763	0.504
TiO_2	0.1859	-	0.1353	0.0069	0.0017	0.082	0.093
ZnO	0.7099	0.1025	0.3875	0.299	0.0551	0.311	0.262
CaO	0.393	0.5452	0.2898	0.3702	0.6351	0.447	0.140
Total	71.1157	55.011	71.4983	74.4824	62.5102		

The following conclusions may be stressed:
- There is no As in the inner part of the particle;
- The highest As concentration is found at point 10 and belongs to the external sorption layer; point 9 is also included in the same layer;
- In the sorption layer located in the opposite side of the particle (points 6 and 7) concentrations are relatively homogeneous but lower than in the opposite face.
- This suggests that chemisorption prevails in relation to the other possible precipitation mechanisms.

This research proves that IBS may be used as reactive media in PRB. The two commercial sorbents tested, ARM 300 and GEH 102, remove efficiently both As(III), As(V) and their mixtures. As(V) is removed easier than As(III). Breakthrough curves obtained in different operating conditions allowed comparing both sorbents: the loading capacity is similar, around 20 g of As/ kg, and GEH has a slightly more favourable performance. Particles of the sorbents, after subjected to adsorption tests in fixed bed columns during 30 days, were subjected to analysis using an electron microprobe analyzer. Spatial mapping of the concentrations allows infer that the removal mechanisms are different: while for ARM 300 reductive precipitation is relevant for GEH 102 the adsorption mechanisms with complex formation are prevalent.

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