Presentation 08/09/2005

Arsenic removal by Zero Valent Iron:

Influence of pH and Redox Potential

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Aknowledgments

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Background

What is Arsenic ?

- Arsenic forms in water

→ Arsenate As(V): H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}

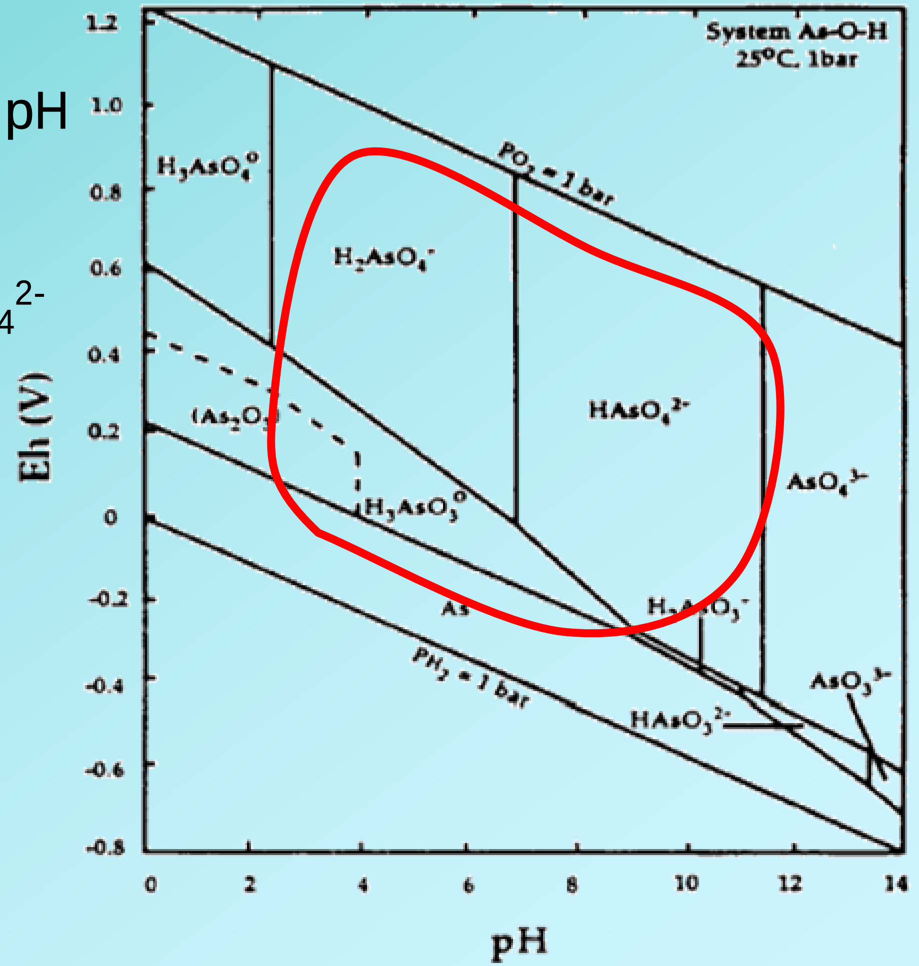
→ Arsenite As(III): H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$ and AsO_3^{3-}

- Arsenite more mobile and toxic than Arsenate

Background

Predominant forms at pH range 5 to 9:

- As(V): $H_2AsO_4^-$, $HAsO_4^{2-}$
- As(III): H_3AsO_3



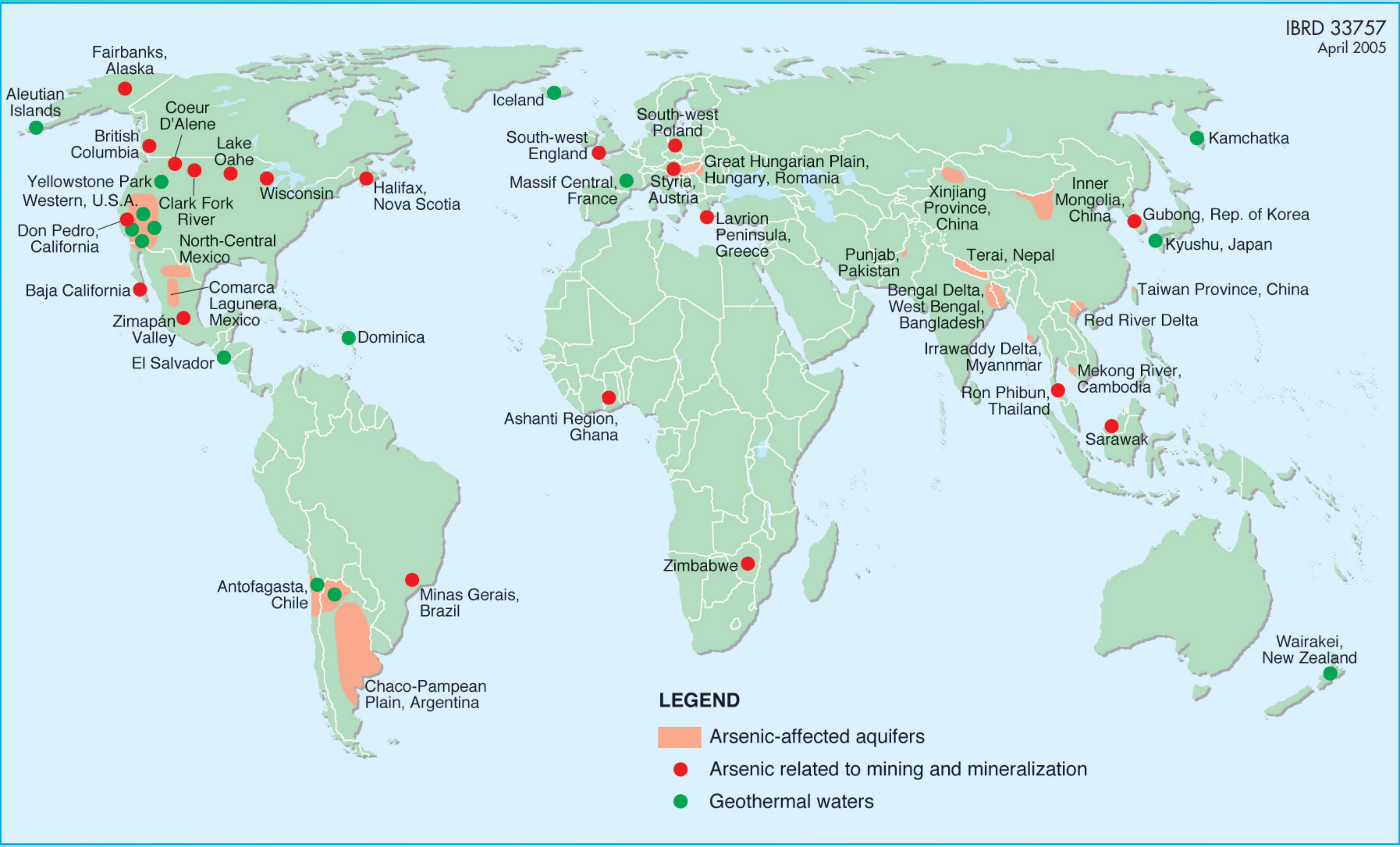
Background

What is Arsenic ?

- **Toxicity:** Cancer (skin, bladder, lung…), Cardiovascular disease, Immunological disorders, Diabetes …

⇨ Regulations since 2003: [As]< 0.01mg/L

Where to find Arsenic ?



Background

Why interest ourselves in Arsenic?

→ World wide problem

→ Concentration range:

0.01 mg/L < [As] < 5 mg/L

→ Probably more than 50 000 000 people are threatened by a chronic Arsenic poisoning.

"Bangladesh is grappling the largest mass poisoning of a population in history... the scale of this environmental disaster is greater than any seen before"

World Health Organization, 09/08/2000

Background

What to do?

⇨ Find a way to treat Arsenic

- Efficient over a wide range of concentration
- Cheap
- Simple

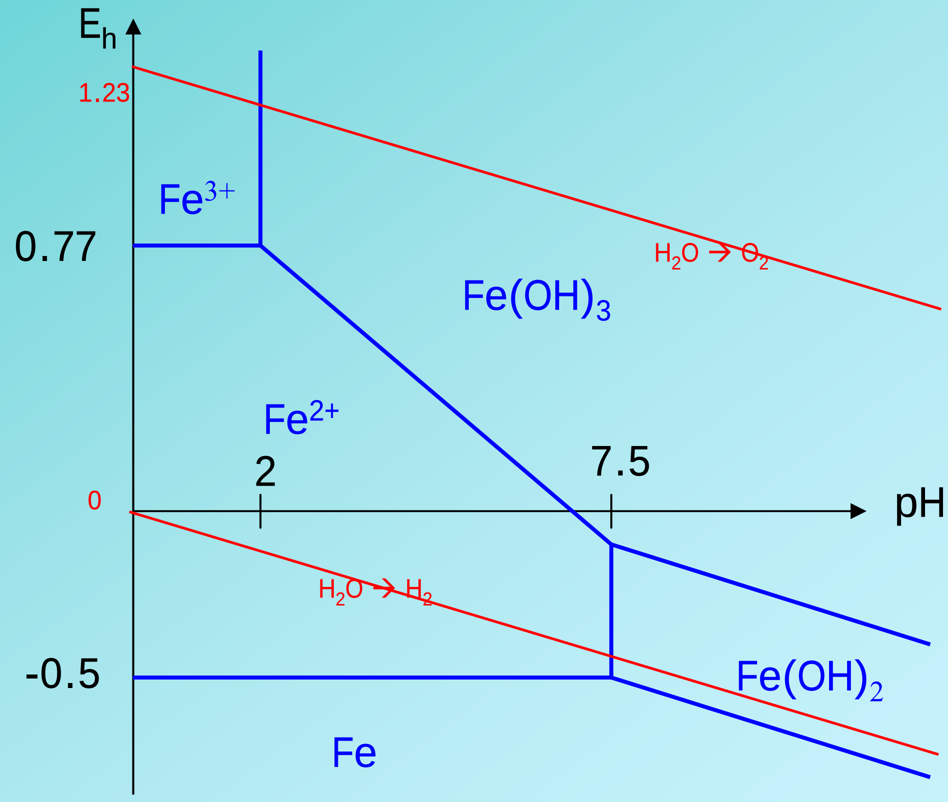
Background

Previous researches

- Different adsorbents (AA, GFH, Goethite…)
- ZVI (mostly since 1999)
  - → Efficiency generally more than 95%
  - → Kinetic
  - → Anions competition
  - → Influence of oxidation state
  - → Mechanism

Background

Diagram E_h-pH for Iron



ZVI present in reductive atmosphere

Study Objectives

- Subject

Arsenic removal by Zero Valent Iron (ZVI): Influence of pH and Redox Potential

- Objectives

→ Assess the efficiency of ZVI to remove Arsenic

→ Test different pH/E_h conditions

→ Evaluate Sulfate competition with Arsenic

Materials and Methods

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Experimental approach:

→ Orthogonal array

Trial	Factors		
	pH	E_h (mV)	Sulfate
1	5	+	+
2			-
3		-	+
4			-
5	6	+	+
6			-
7		-	+
8			-
9	7	+	+
10			-
11		-	+
12			-
13	8	+	+
14			-
15		-	+
16			-
17	9	+	+
18			-
19		-	+
20			-

Materials and Methods

Principle

- pH influence
  - ⟶ Injection of Acid or Base to control pH (V<35mL)
  - ⟶ pH range: 5-9

- E_h influence
  - ⟶ N_2 or O_2 bubbling
  - ⟶ E_h range: Low to High

Materials and Methods

Reactants

- **Arsenic** from As standard 1000 mg/L

  → 3.22 mg/L

- **ZVI** Peerless sieved <0.3mm

  → 200 mg/L

- **Sulfate** Na_2SO_4

  → 250 mg/L

- **Salt** NaCl

  → 0.005 M

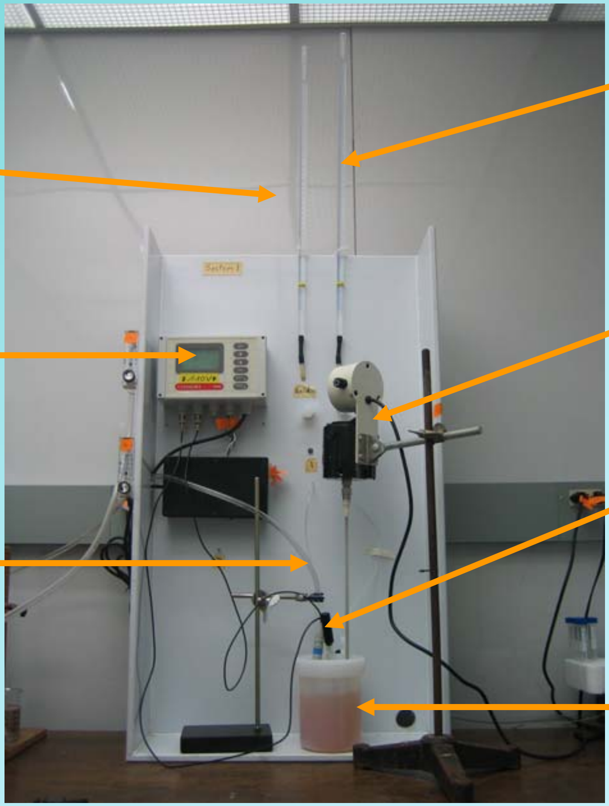
Materials and Methods

Experimental setting

Base

pH Controller

Gas bubbling



Acid

Mixer

Probes

Teflon Beaker

Materials and Methods

Process

1. Overnight ZVI, salt and RO water with gas bubbling. Addition of Sulfate for the competition study

2. Injection of Arsenic in the morning

3. Samples after 10 min, 30 min, 1h, 2h, 3h, 5h

   $V < 10\% V_{initial} \longrightarrow$ limited volume

Materials and Methods

- Samples

  → Filtered and Conserved with 2 drops of HNO_3 in the fridge

  → About 11 mL each

- Analyses

  → Dissolved Arsenic and Iron

  → Private laboratory

  → Method : EPA 200.7 with direct aspiration

  → Detection limit 0.016 mg/L

- Control

  → pH and Eh values recorded and calculus of the standard variance

Results

Results

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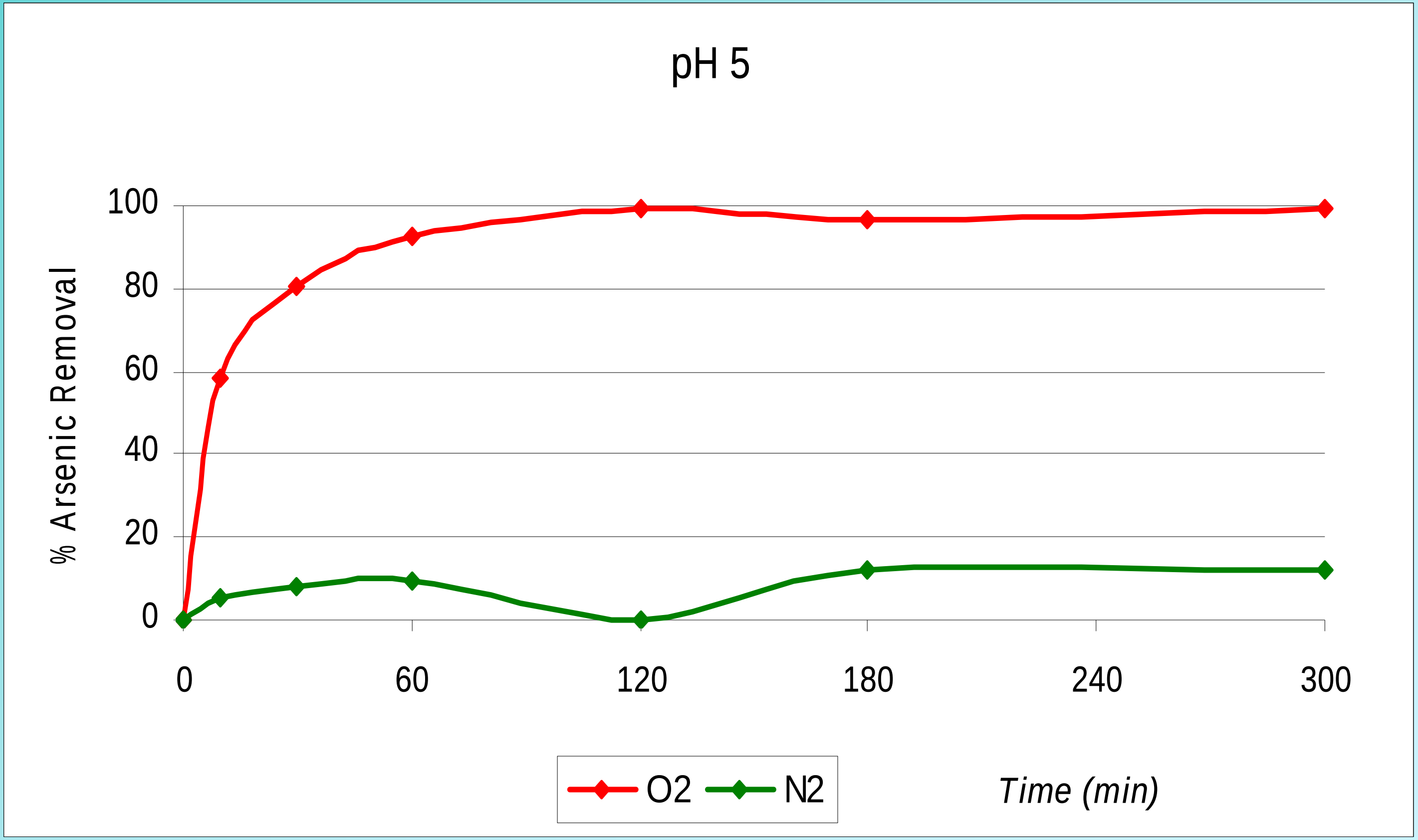
Nantes

- Kinetic studies
  → Time to reach the steady state
- Influence of pH/E_h on the removal
- Sulfate competition
- Data analysis (ANOVA)
- Modeling

Results

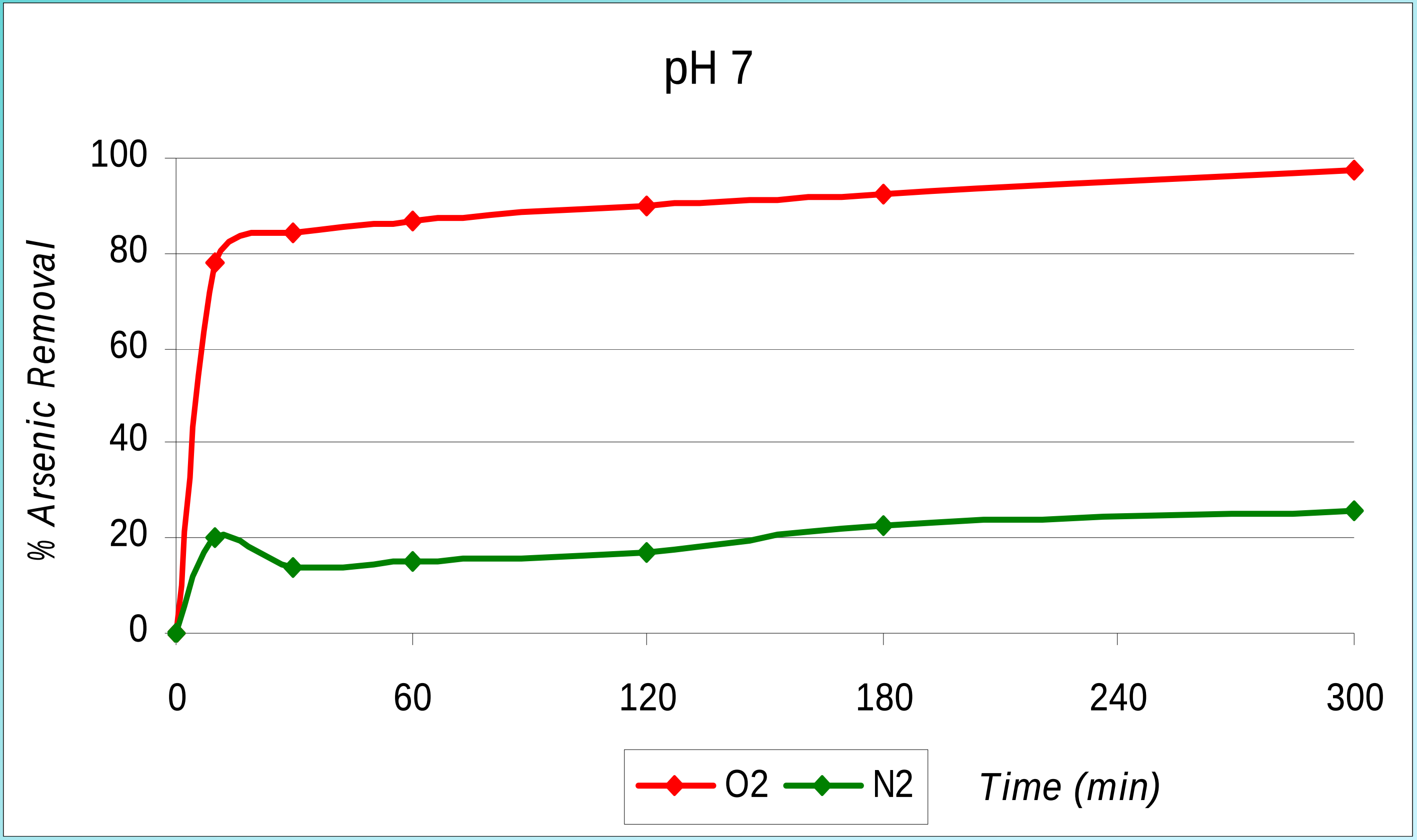
Example of results



Results

I. Background
II. Study Objectives
III. Materials and Methods
IV. Results
V. Conclusions

Example of results



Results

Kinetic studies

- Time to reach the steady state
  → Between 30 to 120 min

- Reaction very quick with O_2
  → pH 5: 80.62% removal after 30 min
  → pH 6: 50.93% removal after 30 min
  → pH 7: 77.70% removal after 10 min
  → pH 8: 75.31% removal after 10 min
  → pH 9: 51.55% removal after 30 min

Results

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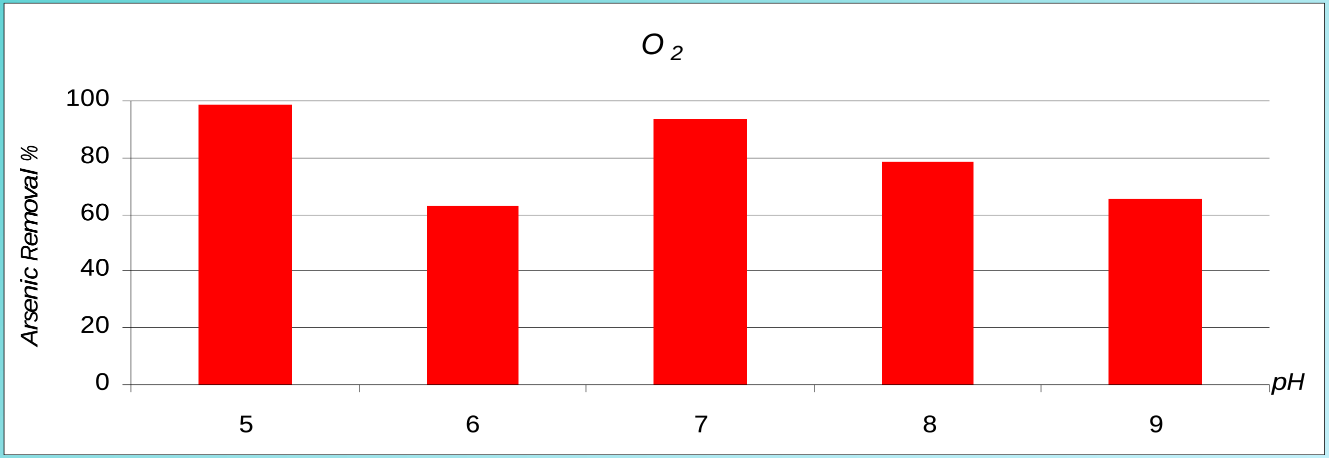
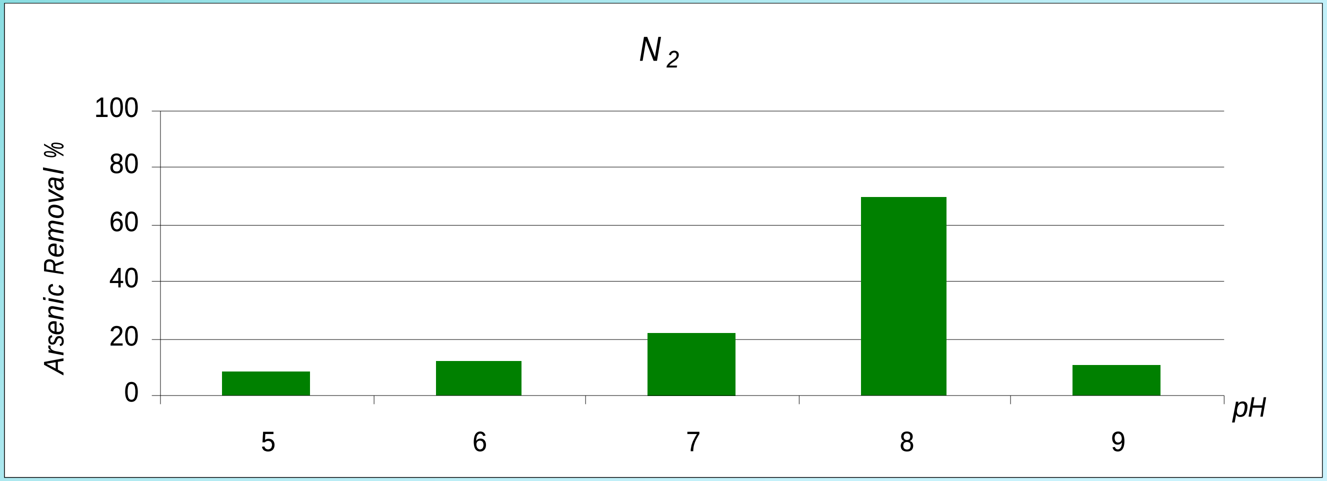
Influence of pH and E_h





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Results

Influence of E_h

Always less than 22 % removal with nitrogen bubbling except for pH 8 (70.03 %)

Always more than 63 % removal with oxygen bubbling

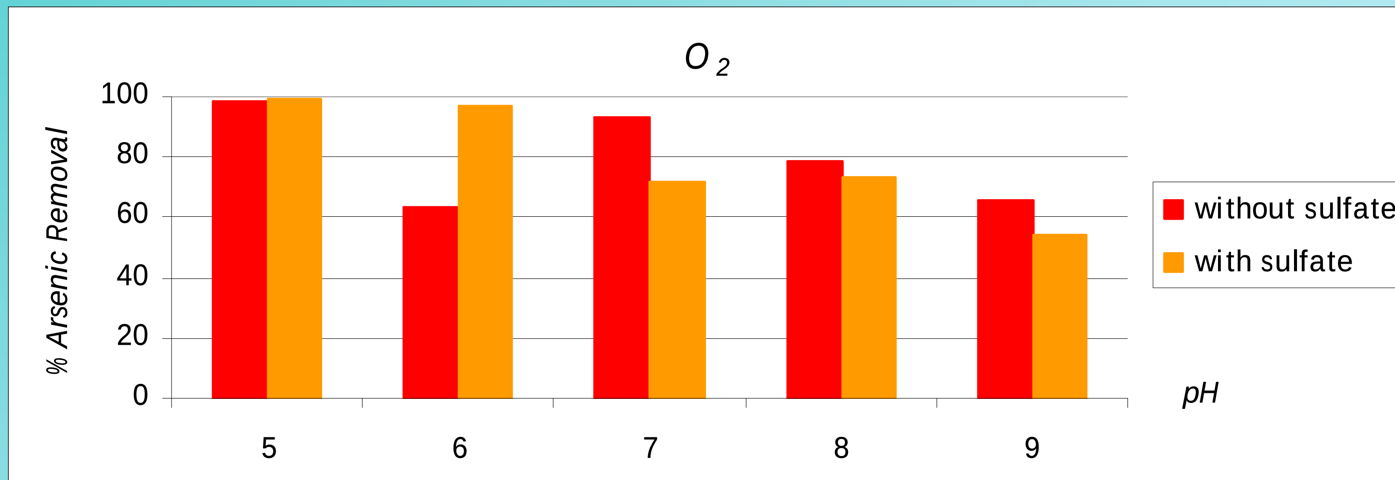
→ Importance of the oxidation state of the Iron.

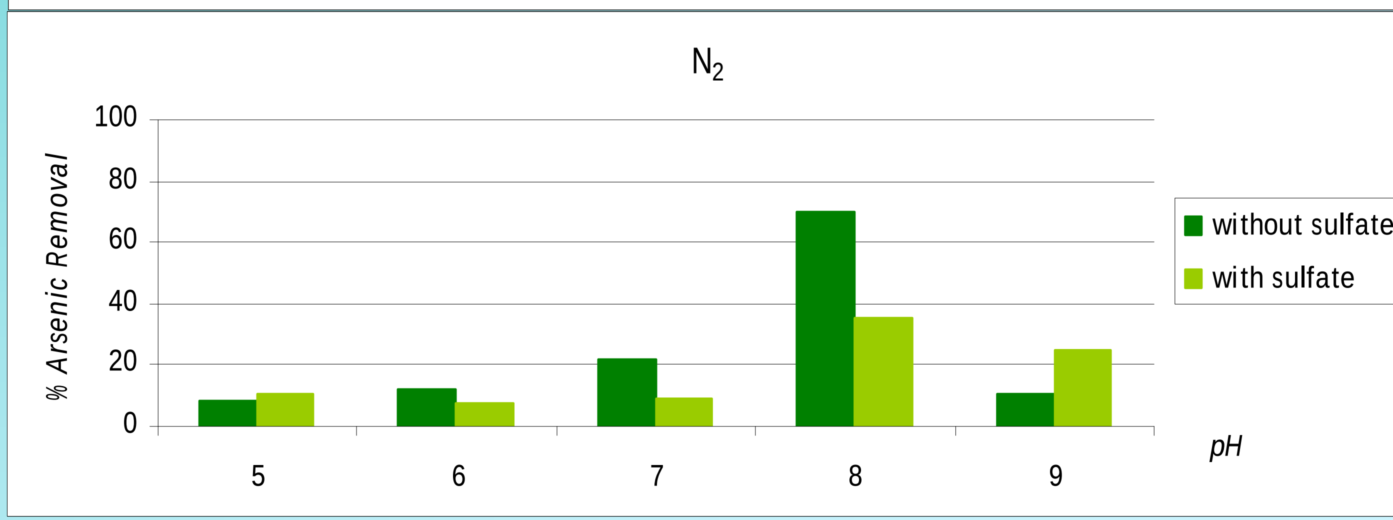
Influence of pH

- With O_2: Higher removal at pH 5
- With N_2: Better removal at pH 8

Results

Competition with sulfate





Results

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Competition with sulfate

Sulfate not very influent

- With O_2

  → Higher competition at high pH

  → Removal slightly improved at low pH

- With N_2

  → Higher competition at low pH

  → Removal slightly improved at pH 9

Results

Conditions pH	Conditions E_h	Without Sulfate Arsenic Adsorption Density (mg/g)	With Sulfate Arsenic Adsorption Density (mg/g)
5	O_2	15.72	15.95
	N_2	1.31	1.69
6	O_2	10.21	15.59
	N_2	1.95	1.24
7	O_2	15.13	11.61
	N_2	3.49	1.40
8	O_2	12.50	11.79
	N_2	11.31	5.71
9	O_2	9.31	8.68
	N_2	1.69	4.05

Results

Analysis of Variance (ANOVA)

Source	DF	Sum of Squares	F Ratio	Prob > F	Contribution %
Redox	1	429.20112	55.6989	<.0001	86.27
pH*Redox	1	58.03281	7.5311	0.0178	11.41
pH	1	2.28484	0.2965	0.5961	0.2
Redox*Sulfate	1	2.05440	0.2666	0.6150	0.1
pH*Sulfate	1	1.90969	0.2478	0.6276	
pH*Redox*Sulfate	1	1.18336	0.1536	0.7020	2
Sulfate	1	1.20541	0.1564	0.6994	

Results

Modeling with Jump

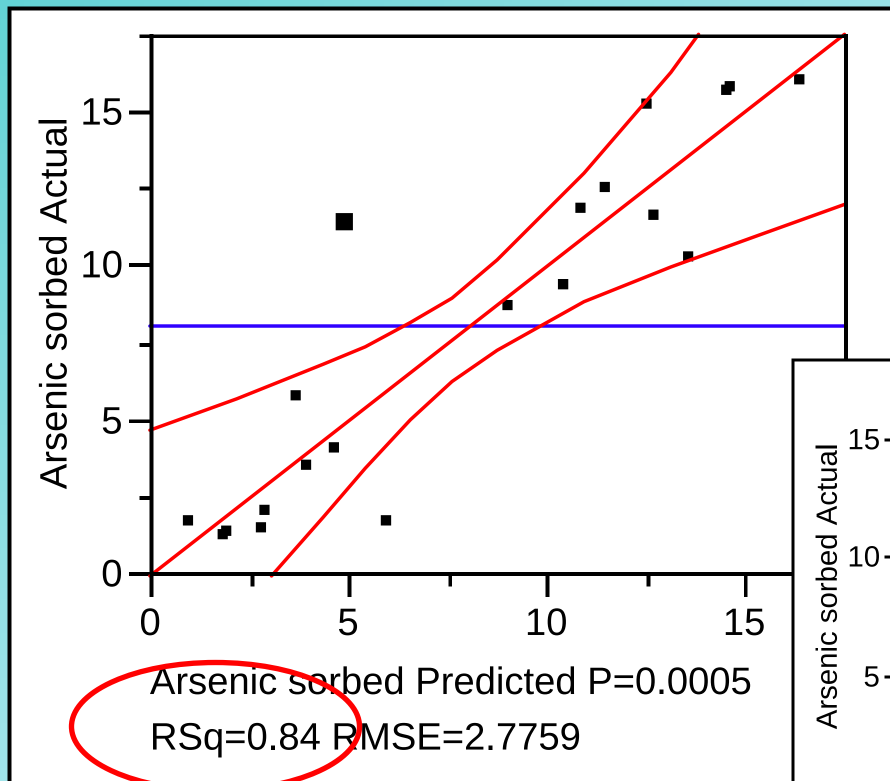
- **Output:** Arsenic Adsorption Density (mg/g)
- **Input:** pH, E_h, Sulfate
- Model defined by the following coefficient:

Term	Estimate	Std Error	t Ratio	Prob>|t|
Intercept	9.6895	3.134456	3.09	0.0093
pH	-0.239	0.438912	-0.54	0.5961
Redox[1]	-4.6325	0.620715	-7.46	<.0001
Sulfate[1]	0.2455	0.620715	0.40	0.6994
(pH-7)*Redox[1]	1.2045	0.438912	2.74	0.0178
(pH-7)*Sulfate[1]	0.2185	0.438912	0.50	0.6276
Redox[1]*Sulfate[1]	0.3205	0.620715	0.52	0.6150
(pH-7)*Redox[1]*Sulfate[1]	-0.172	0.438912	-0.39	0.7020

→ [As] =9.69 -0.24 pH – 4.63 Redox[1] – 0.25 Sulfate [1] …

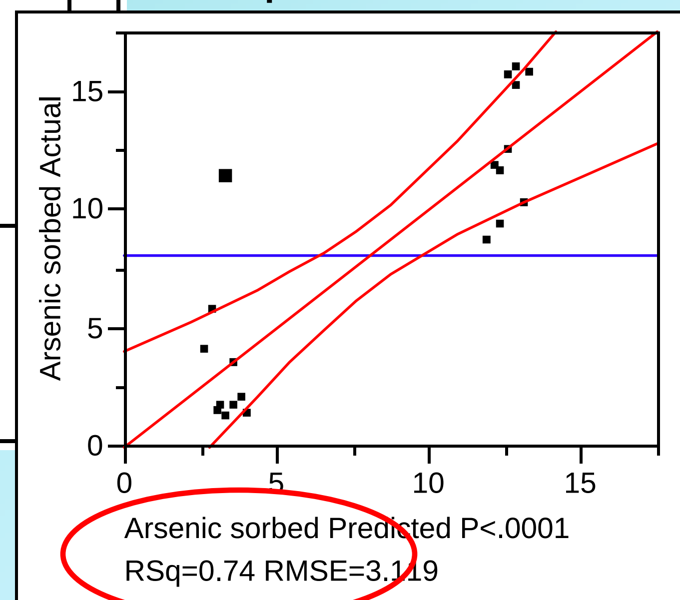
Results

Efficiency of the model



Full Model

Simplified Model



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Results

Results of the model

Influence of each factor on Arsenic removal

If we have…

			Low pH	High pH	Low E_h	High E_h
What is the effect of…	↗pH	No Sulfate			↗↗↗	↘↘
	↗E		↗↗↗	↗↗		
	↗pH	With sulfate			↗↗↗	↘↘
	↗E		↗↗↗	↗↗		

Legend: ↗ + 0 to 25 % ↗↗ + 25 to 100 % ↗↗↗ + > 100 %

↘ - 0 to 25 % ↘↘ - 25 to 100 % ↘↘↘ + > 100 %

Conclusions

Conclusions

- Kinetic Study

  → Quick reaction: 30 to 120 min

- Influence of Redox potential

  → Removal more efficient with Oxygen

  WHY? Formation of fresh oxides

- Influence of pH

  → With O_2: Increasing pH has a negative effect

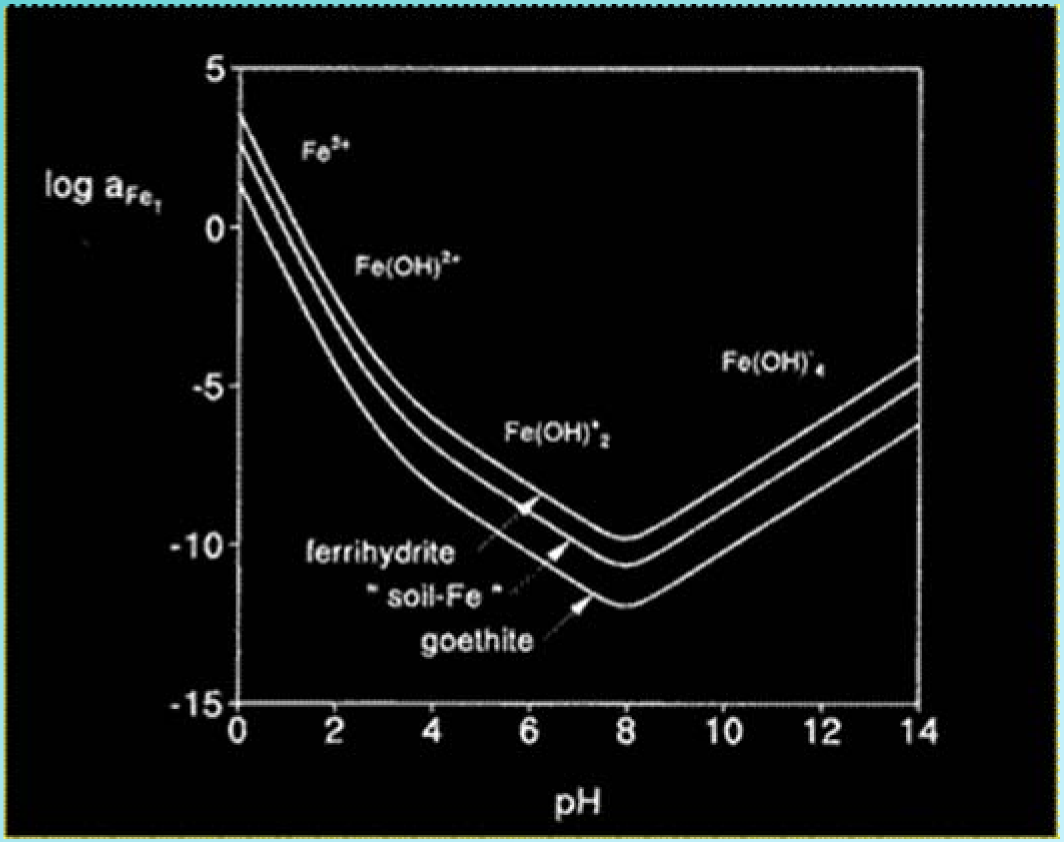
  WHY? Competition with OH^-

  → With N_2: Better removal at pH 8 (with or without sulfate)

  WHY?

Conclusions

Solubility of iron hydroxides as a function of pH



Ferrous oxides more efficient than ferric oxides

Conclusions

- Sulfate competition

  → Not a very important action

  → Higher competition at high pH with O_2

  → Improve the removal at low pH with O_2

Recommendations

Independent data to validate the model

More studies needed at various Redox levels

Further studies at pH 8 (pH 8, Eh low)

Additional competition studies needed at various pH/E_h conditions

Influence of L/S ratio

Questions?