Case Study:
Using Hydrous Ferric Oxide to Remediate Dissolved Arsenic

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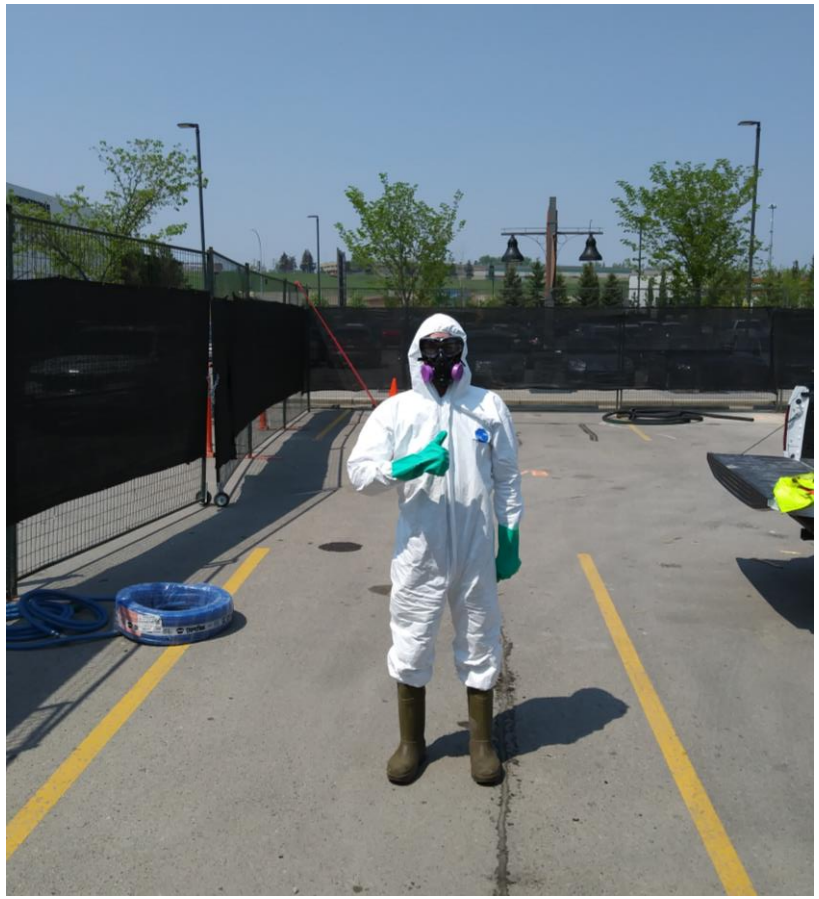
LANGAN

Health and Safety Moment

- Ferrous Sulphate Dust
- Oxidants
- Chemical Reactions
- Pressurized equipment
- PPE for the job
  - NIOSH-fitted respirator
  - Wrist-length gloves
  - Tyvek suit
  - Goggles
  - Chem-resistant boots



Outline

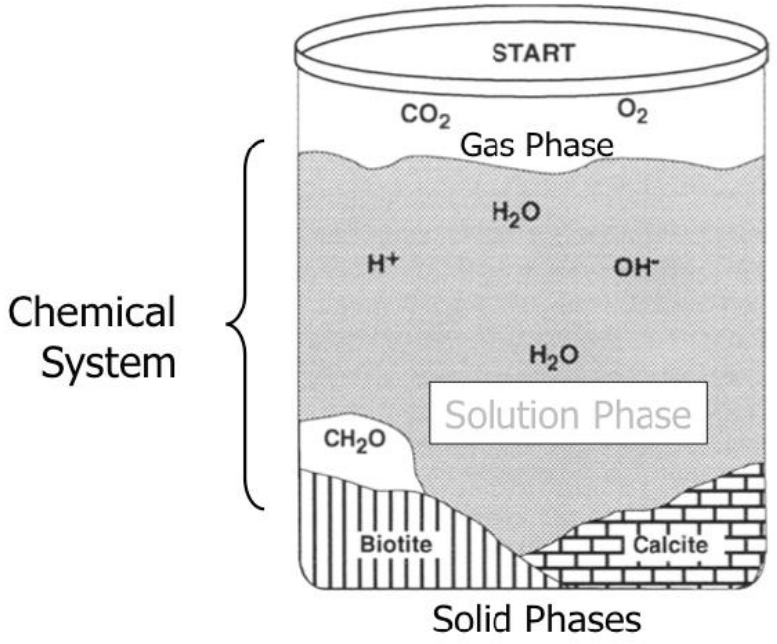
- Introduction
- Definitions
- Iron and Other Reactive Minerals
- Iron Geochemistry
- Analytical Methods
- Case Study
- Conclusions
- Questions

Introduction

- Geological Engineer, Hydrogeologist, Geochemist?
- 15 years experience in consulting
- Langan International LLC ~1 year
- 10 years of experience with metals remediation
- Langan 25+ years experience with metals remediation
  - ZVI and HFO; ISCO & ISCR

- Feed your metals contamination; augment aquifer solid phase

Definition – Aquifer Solid Phase



Source: NWGA Short Course

- Soil Sample ≠ Solid Phase Characterization
- BUT
- Solid Phase Characterization = Soil Sample

Definitions - Reactive Minerals?

- Minerals that dissolve and/or re-precipitate within a human time-scale in response to changes to pH, redox, or solution composition
  - Solution controls (i.e. saturation)
  - Minerals equilibrium F(pH, Eh, solution composition)
  - Adsorbent surface for metals
  - Sources and sinks

Iron and Other Reactive Minerals

- HFO – Hydrous Ferric Oxide or Iron Oxyhydroxide aka “rust”
  - Fe(III) with varying amounts of O^{2-} and H^{+}
  - ferrihydrite [$Fe(OH)_3$], goethite [$\alpha FeOOH$], etc.
- Dzombak and Morel (1990) up to 600m^2/g surface area for ferrihydrite!

Iron and Other Reactive Minerals

- Other Adsorbents
  - Manganese oxides: pyrolusite [MnO_2]
  - Aluminum hydroxide: gibbsite [$Al(OH)_3$]
  - Clay and organic carbon minerals (not *technically* reactive minerals)

- Solubility Controls
  - Salts: halite [NaCl], $MgCl_2$, KCl, gypsum [$CaSO_4 \cdot 2H_2O$]

Iron and Other Reactive Minerals

- Buffering Agents
  - Limestone: calcite [$CaCO_3$], dolomite [$CaMg(CO_3)_2$]

- Sulphide (Acid Rock Drainage)
  - Sulphides: pyrite [FeS_2], galena [PbS], sphalerite [(Zn,Fe)S], etc.
- Acid Rock Drainage is a result of oxidation of reactive minerals
- Metals plume after injection of chemical oxidant?

Iron Geochemistry

- HFO is nearly ubiquitous (~500 mg-Fe/kg-soil)
- HFO Physical Properties
  - Ferrous Fe(II) highly soluble (~ g/L)
  - Ferric Fe(III) relative insoluble over a range of pH/Eh conditions
    - Dissolve under reducing conditions
  - Structure: amorphous, cryptocrystalline, crystalline
    - Evolves over time
  - Form reaction rims
    - Surface area

Iron Geochemistry

General Affinity of Dissolved Species for $Fe(OH)_3$

$As^{5+} = Cu^{2+} = Be^{2+} = Pb^{2+} = PO_4^{3-}$

$> Zn^{2+} > Cd^{2+} > As^{3+} > Ni^{2+} > SO_4^{2-}$

$>> Ba^{2+} >> Ca^{2+} >> B^{3+}$

Also Co^{2+}

$SeO_3^{2-} > SeO_4^{2-}$ Research ongoing

Arsenate (As^{5+}) most strongly adsorbed, boron least strongly adsorbed

Iron Geochemistry

- Inject ferrous sulphate heptahydrate ($FeSO_4 \cdot 7H_2O$)
- Oxidize ferrous (II) to ferric (III)
- Precipitate HFO
- Increasingly crystalline over time as O to H ratio increases

Iron Geochemistry

+

=

Iron Geochemistry

- Coprecipitate and Adsorb metals
  - $2FeSO_4 + 1/2O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 2H_2SO_4$
    - Reaction needs pH neutralization – sufficient limestone present?
    - O_2 required to oxidize ferrous iron to ferric iron – natural oxidant present?
  - $\equiv FeOH^+ + Cu^{2+} \rightarrow \equiv FeOCu^{2+} + H^+$

Analytical Techniques

- Solid Phase Characterization?
  - Batch sequential extraction (Tessier)
  - Column sequential extraction (modified Tessier)
  - Polished thin-sections
  - SEM-EDS
  - QEMSCAN

Batch Sequential Extraction

- Tessier (1979)
  - 1 – Exchangeable cations: magnesium chloride/sodium acetate
  - 2 – Carbonates: acetic acid
  - 3 – Fe/Mn oxyhydroxides: hydroxylamine hydrochloride
  - 4 – Organics: hydrogen peroxide
  - 5 – Aqua Regia: sulphuric acid
- Limitations:
  - Small sample mass/volume
  - Reaction Kinetics

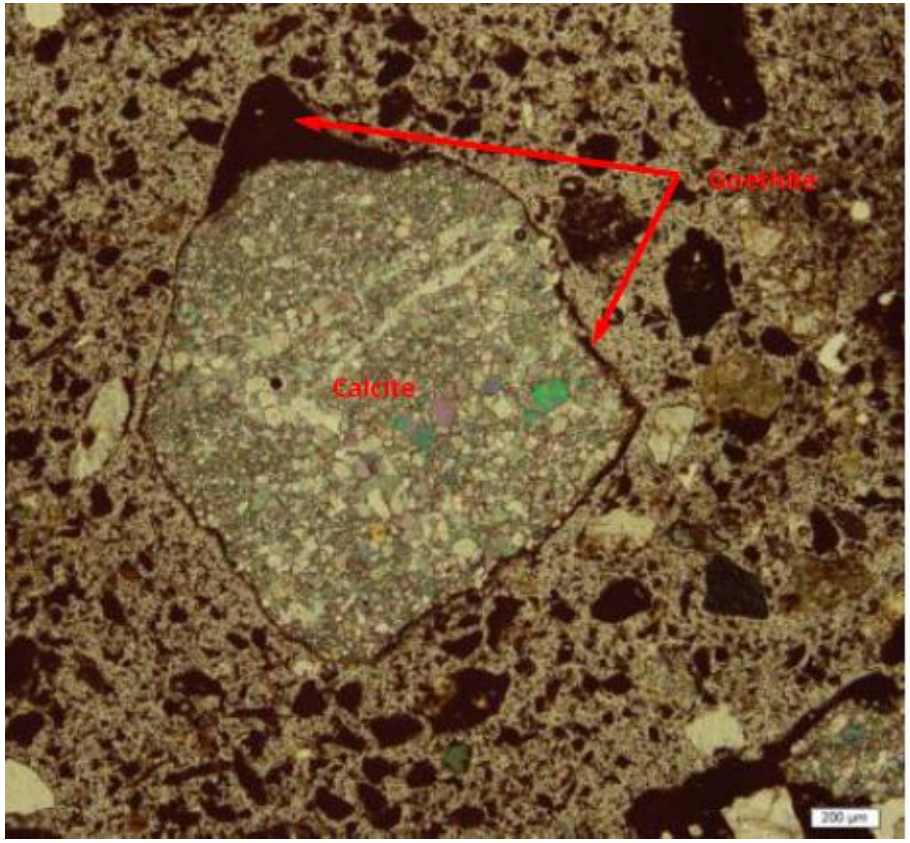
Column Sequential Extraction

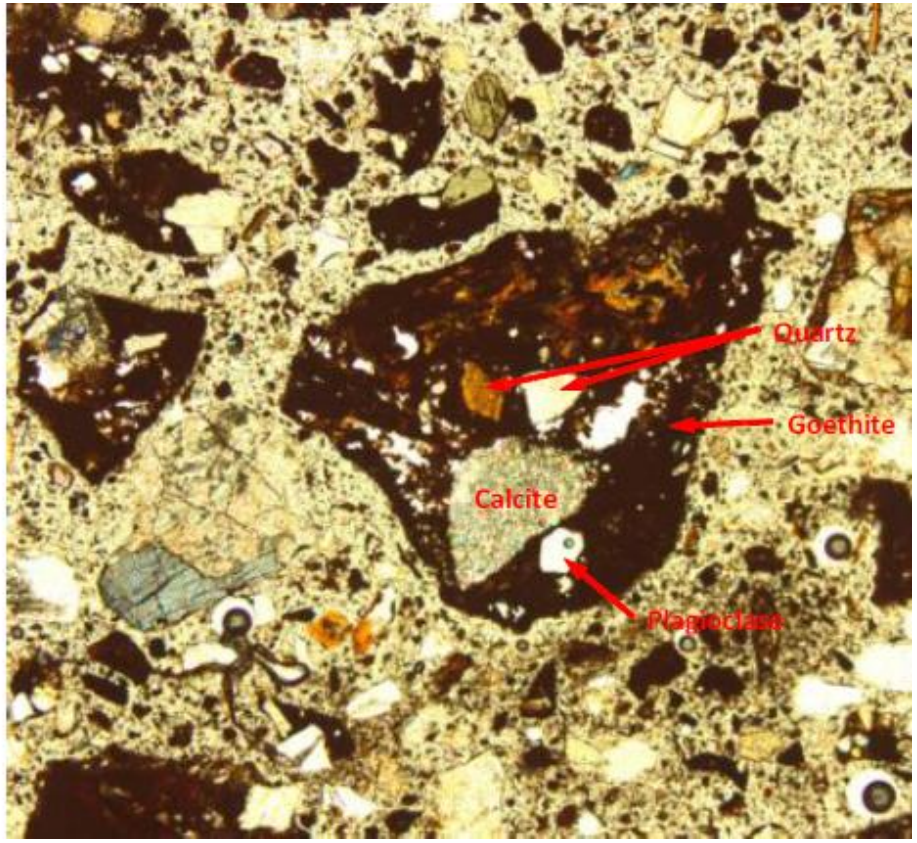
- Modified Tessier
  - 1 – Water Soluble: DI water
  - 2 – Exchangeable: ammonium chloride
  - 3 – Carbonates: sodium acetate + acetic acid
  - 4 – Fe/Mn oxyhydroxides: ammonium oxalate + oxalic acid

- Mimics reactions along a flow path
- Accounts for reaction rim and reaction kinetics
- Mineral stability across range of geochemical conditions

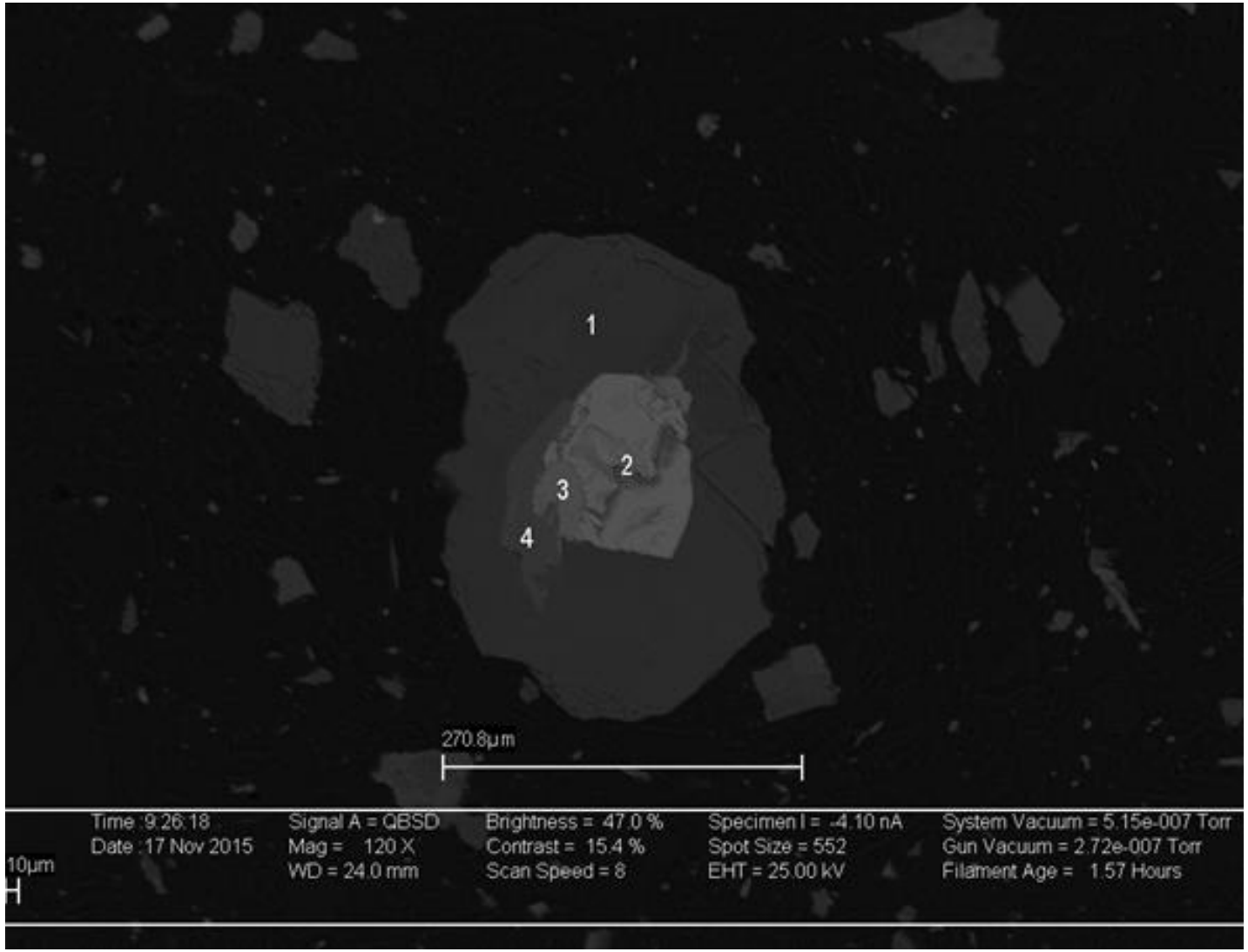
Column Sequential Extraction

Polished Thin-sections





SEM-EDS


1
2
3
4
270.8µm
Time :9:26:18
Date :17 Nov 2015
Signal A = QBSD
Mag = 120 X
WD = 24.0 mm
Brightness = 47.0 %
Contrast = 15.4 %
Scan Speed = 8
Specimen I = -4.10 nA
Spot Size = 552
EHT = 25.00 kV
System Vacuum = 5.15e-007 Torr
Gun Vacuum = 2.72e-007 Torr
Filament Age = 1.57 Hours
10µm
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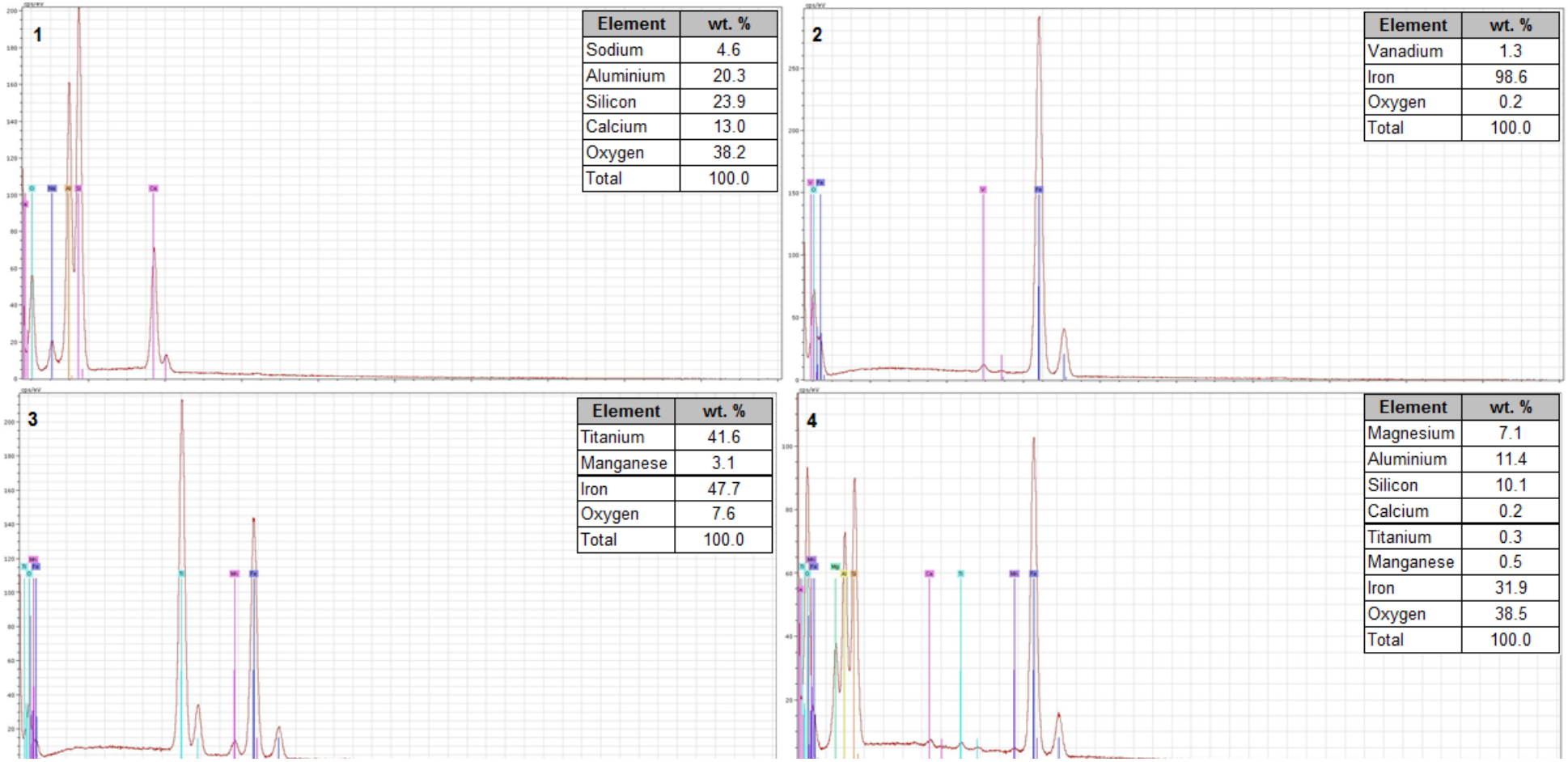
SEM-EDS



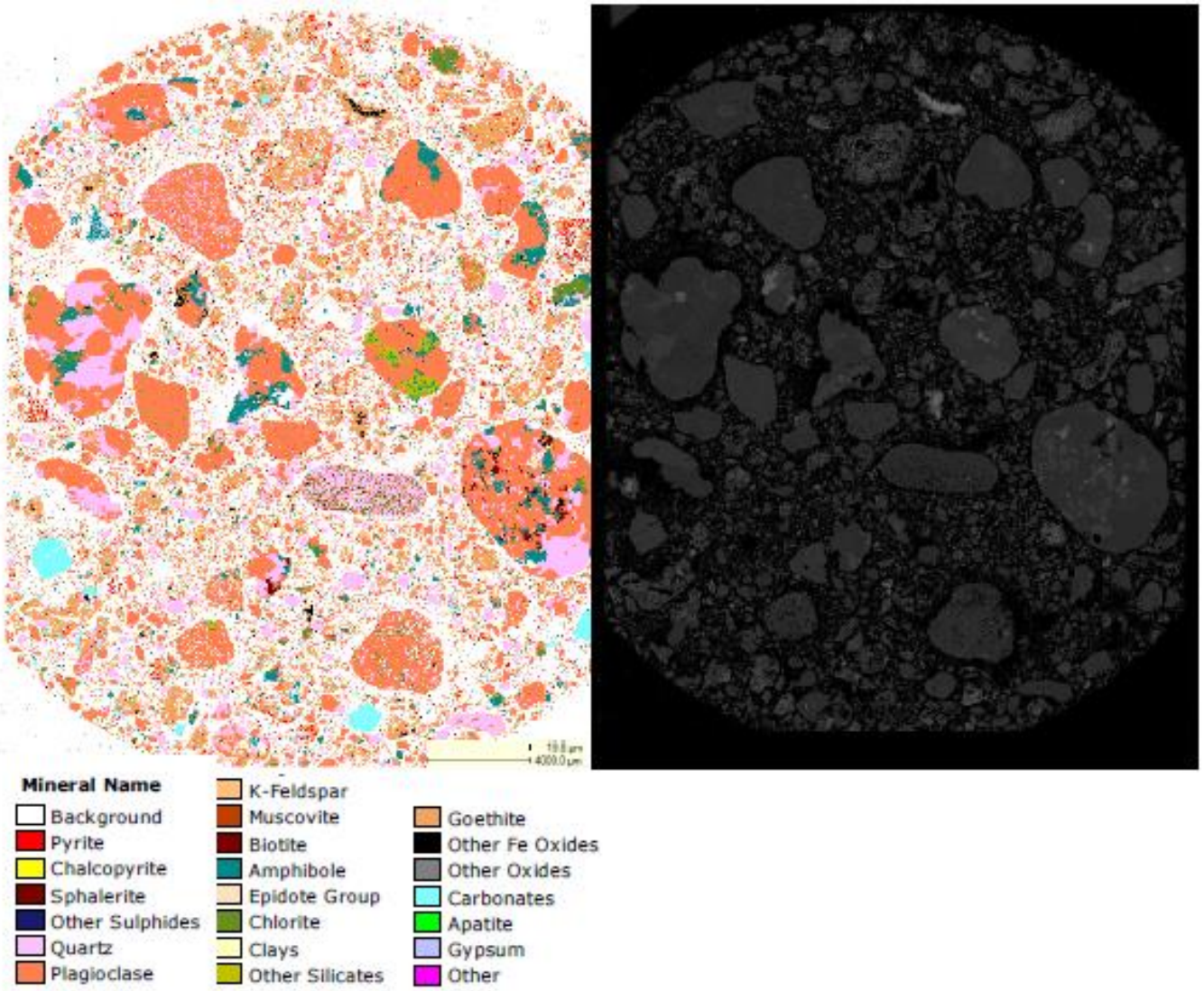
Element	wt. %
Sodium	4.6
Aluminium	20.3
Silicon	23.9
Calcium	13.0
Oxygen	38.2
Total	100.0

Element	wt. %
Vanadium	1.3
Iron	98.6
Oxygen	0.2
Total	100.0

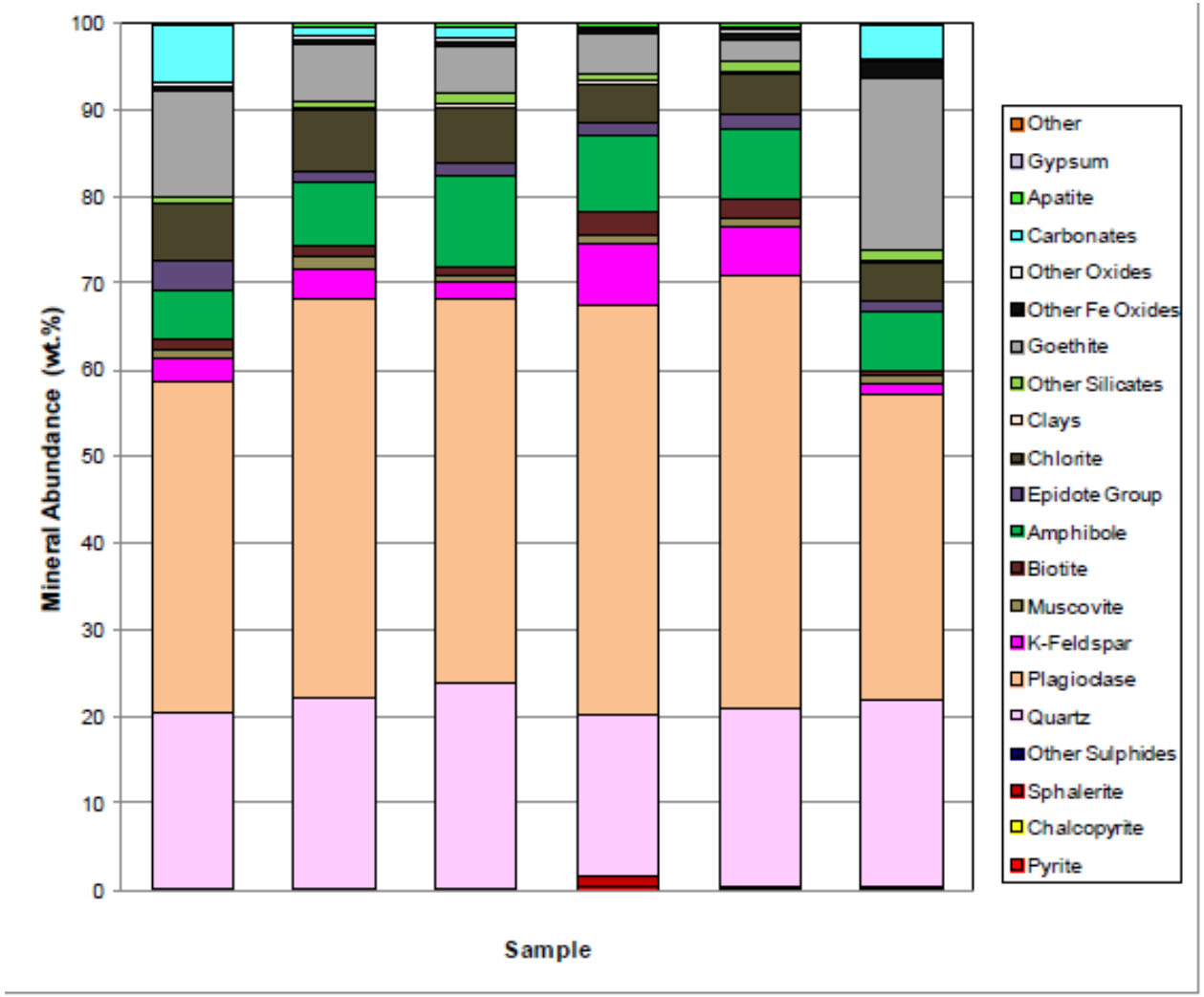
Element	wt. %
Titanium	41.6
Manganese	3.1
Iron	47.7
Oxygen	7.6
Total	100.0

Element	wt. %
Magnesium	7.1
Aluminium	11.4
Silicon	10.1
Calcium	0.2
Titanium	0.3
Manganese	0.5
Iron	31.9
Oxygen	38.5
Total	100.0

QEMSCAN – Automated SEM-EDS



QEMSCAN – Automated SEM-EDS



Case Study

- HFO remediation on few Sites in Canada & numerous sites in the USA
- Often large industrial and/or mining sites
- Multi-parameter plumes
- High concentrations (10’s mg/L)
- Long plumes (100’s m)

Case Study

- Months/Years to characterize Site
- Months/Years to design (bench and pilot scale)
- Extensive equipment required
- Chemical inputs – supply chain/border crossing
- Numerous data inputs
- Weeks/Months to install
- Years of monitoring
- Large budgets >$1M

Case Study – The Site

- Confidential Site in USA
- Small Commercial Property
- Shallow Groundwater (~2 mbgs)
- Small plume ~ footprint of building

Case Study – The Challenge

- Dissolved arsenite (As^{3+}) plume – 150 µg/L
- Minimal design inputs
- Imminent property transaction
- State requires Injection Permit
- Clean Site not Risk Managed
- Maintain building operations

Case Study – The Solution

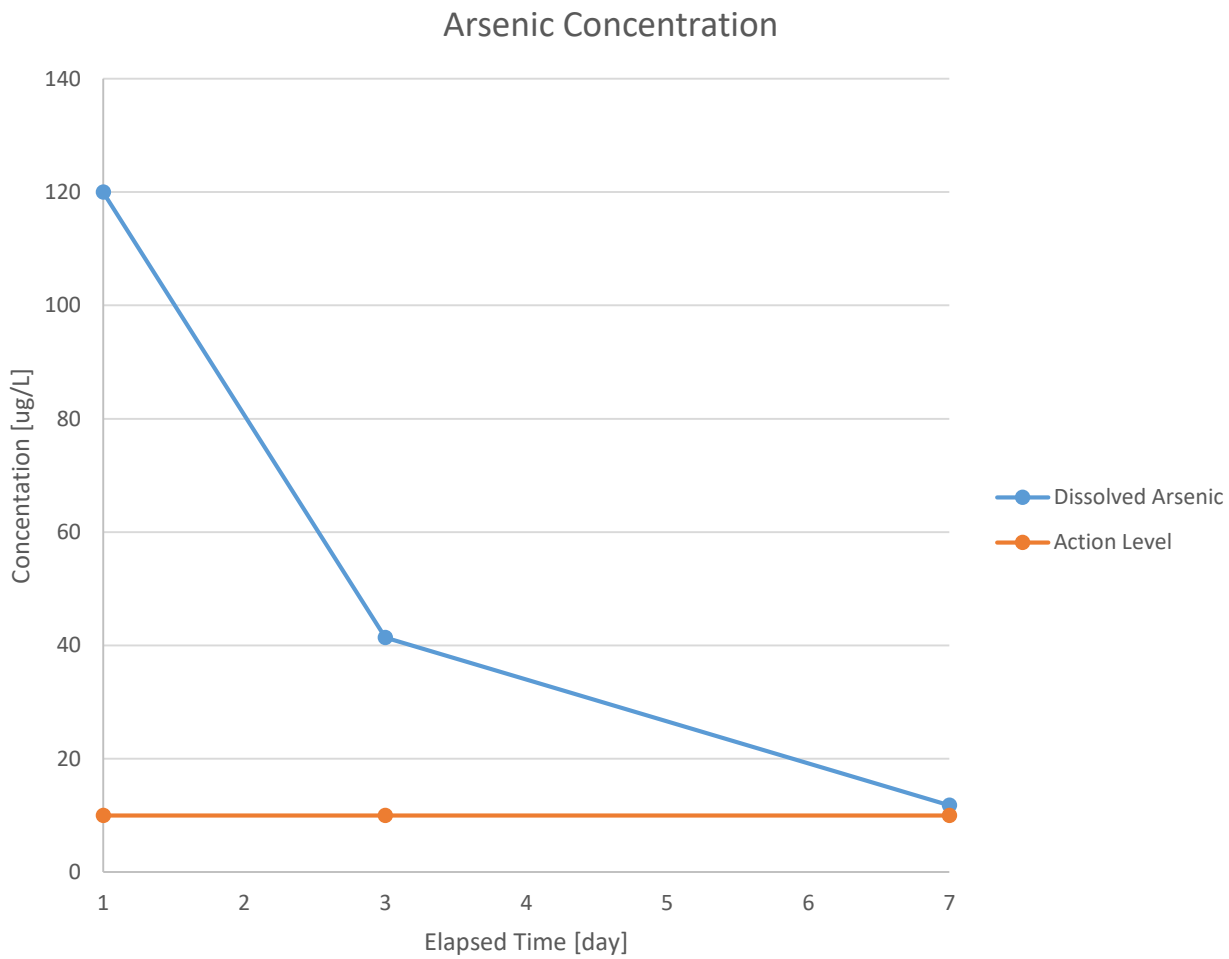
- Feed it!
- Apply understanding of iron geochemistry
  - Oxidizing Aquifer
    - 1 mg/L DO ~ 8 mg/L Fe
  - Abundant Limestone in Aquifer Solid Phase
  - Arsenic only

Case Study – The Solution

- Dissolve 55 kg ferrous sulphate in Site groundwater and inject
- Pump out, re-inject
- Inject O_2 using compressed air into injection well and down-gradient well
- 8hrs/day, 7 days
- Sample 1st, 3rd, 7th day

Case Study – Results

- Decrease arsenic to action level within 1 week
- Decrease in arsenic parallel to decrease in iron
- Property transaction timeline met



Case Study – The Elegance

- Rapid implementation (2 weeks)
- Site uniquely required limited characterization
- Small budget for remediation (~$15,000)
- Total budget ~$50,000

Questions?