Chemistry and Remediation of Arsenic

A View From The Private Sector

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Overview

- Background, General and Environmental Chem
- Water Regulations and Opportunities
- Existing Technologies, Alternative Tech, GFH
- Current Approaches
- Private Sector Views
- Conclusion

Background

- Arsenic- Group V Element (N, P, As, Sb, Bi)
- Exists in nature primarily as oxide or oxy anion
- 20th most abundant element, avg. conc. 2-3 mg/kg
- Most important commercially is As_2O_3
- Health and environmental effects
- Recent FDA approved drug: As_2O_3 …it's the dose!
- Water Regs: Global (WHO) and Domestic (EPA)

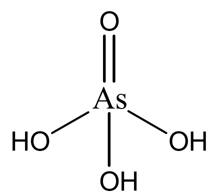
References

"Advanced Inorganic Chemistry", F.A. Cotton and G. Wilkinson, John Wiley and Sons, 1972, ISBN: 0-471-17560-9.

"Environmental Chemistry of Arsenic", W. T. Frankenberger, Jr., Ed., Marcel Dekker, 2002, ISBN: 0-8247-0676-5.

General Chemistry

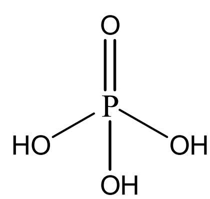
- Behaves similarly to phosphorus, particularly acid-base behavior:



$pK_1 = 2.2$

$pK_2 = 6.9$

$pK_3 = 11.5$



$pK_1 = 2.1$

$pK_2 = 7.2$

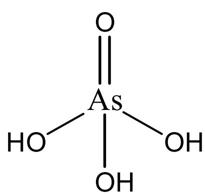
$pK_3 = 12.4$

- As(III) and As(V): As(V) favored at E_h >-100 mV at pH 8 and >300 mV at pH 4

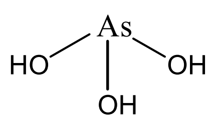
- Primarily +5 in oxidative environments or readily convertible

Environmental Chemistry

Arsenic Compounds Commonly Found in the Environment:

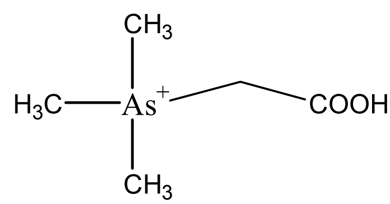


As(V)

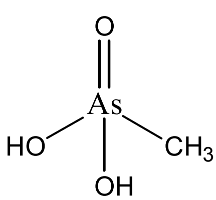


As(III)

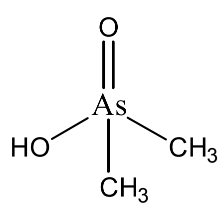
($pK_1 = 9.2$)



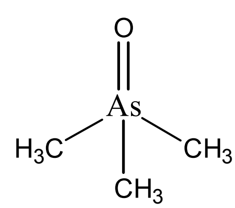
Arsenobetaine (AB)



Methylarsonate (MA)



Dimethylarsonate (DMA)



Trimethylarsine Oxide (TMAO)

$FeAsS$	As_2O_3	Cu_2OHAsO_4	$CoAsS$	Ag_3AsS_3
Arsenopyrite	Arsenolite	Olivenite	Cobaltite	Proustite

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EPA Water Regulations

Due to adverse health and environmental effects- Arsenic levels regulated in potable water and discharges into non-potable water:

• Arsenic Levels in Potable Water:

Currently = 50 ppb (est. 1942)

New Regulations = 10 ppb (2006)

[WHO Guidelines = 10 ppb (1993)]

• Arsenic Discharges into Non- Potable Waters, Generally:

Fresh Water = 36 ppb

Sea Water = 340 ppb

New Regulations – New Opportunities

- Implementation of new regulations: estimated to generate markets in excess of several hundred million dollars for the private sector (>$300 MM).
- Potential Customers: Municipal Water Works, Private Wells, Homeowners, etc.
- Cost sensitive customers.
- Application of existing arsenic removal technologies and alternative approaches.

Existing Technologies

- Coagulation/Filtration (C/F): Essentially precipitation and filtration processes (alum, ferric salts, lime, etc.).
- Adsorptive Processes: Primarily alumina (Al_2O_3) and related analogs.
- Ion Exchange: Synthetic resins and related.
- Membrane Processes: microfiltration, ultrafiltration, nanofiltration.

- Primary Driving Force: Lower Costs

Alternative Approaches

• Primarily Iron(III) Based or Related Technologies:

- Iron oxide coated substrates (sand, alumina, etc.)

- Precipitation iron oxides and related

-Granular ferric hydroxide: $Fe(OH)_3$

• Currently, GFH (Granular Ferric Hydroxide) is choice or benchmark.

• Again, Primary Driving Force: Lower Costs

Granular Ferric Hydroxide

- Typically prepared by alkaline precipitation of ferric hydroxide from ferric chloride:

$$FeCl_3 + 3NaOH \rightarrow Fe(OH)_3 + 3NaCl$$

- It's cheap, plentiful and it works.
- Arsenic removal ranging from about 5 mg of arsenic per gram of GFH to 50 mg/g.
- Problem: GFH is a granular material that is relatively non-robust and susceptible to particle fracture, attrition, and bed-cracking, i.e, materials properties issues
- Better material would also incorporate "ease of use".
- Yet Again, Primary Driving Force: Lower Costs

Alternative GFH Approaches

• GFH precipitation and entrapment in robust, porous solids.

• Client Company: SolmeteX, Inc.

• Using Synthetic Resins (IEX and Related) and precipitation of iron oxides from dissolved ionic iron species by:

- Manipulation of pH

  (Fe^{3+} insoluble at pH >3)

- Manipulation of redox

  (Fe^{2+} insoluble at pH >5)

• Currently good results.

A View From the Private Sector

- Unlike businesses in other sectors, not market driven or technologically driven- but “statutorily driven”
- Generally, customer does not want to buy your product but is required (regulations or statutes).
- Translates into stiff cost competition- low margins, low growth.
- Sales are usually at last minute and to lowest cost provider- rarely loyal customer base.
- General reluctance to change
- Upon graduation, working in private sector- upfront think about environmental impact and sustainability.

Chemistry
The Central Science

• A proper basis and understanding of chemistry is central to successfully resolving environmental issues.

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Special Thanks to Jessica Brooks

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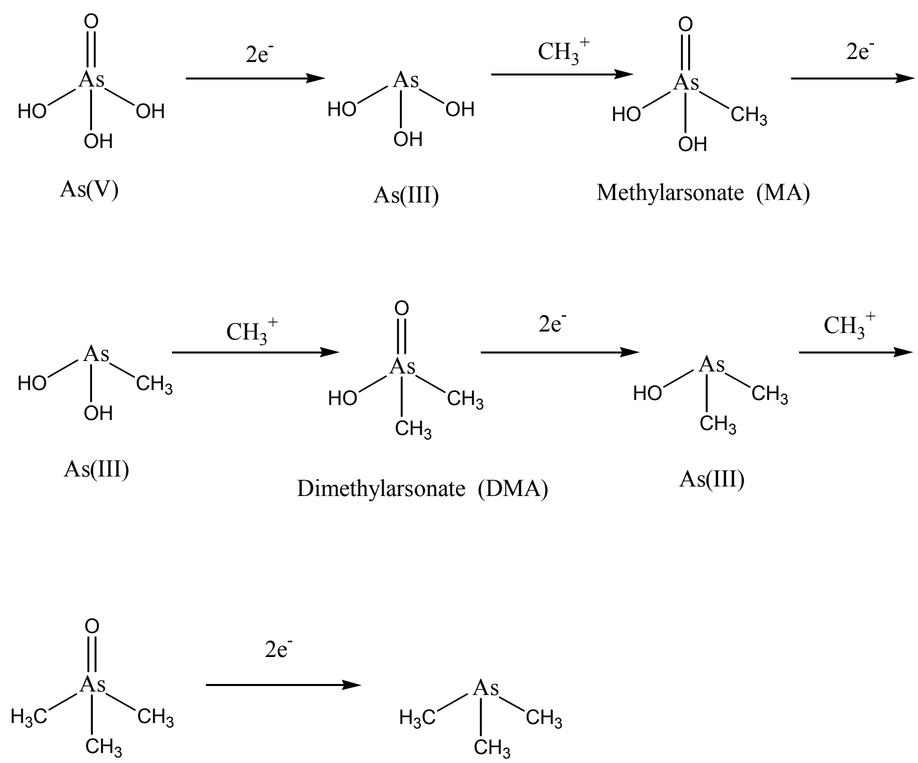
Arsenic Metabolism

The metabolism of arsenic primarily involves reduction of pentavalent arsenic to trivalent arsenic by arsenate reductase and methylation of trivalent arsenic to monomethylarsonic acid and monomethylarsonic acid to dimethylarsinic acid by methyltransferases. The main site of methylation reactions appears to be the liver. Arsenic is stored mainly in liver, kidney, heart, lung, hair and nails.



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