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Pilot-Scale Evaluation of Adsorptive Media for Arsenic Removal

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August 10, 2004

Acknowledgement

- Funding provided by U.S. EPA under the Physical/Chemical R&D Support Contract (No. 68-C7-0008) and Field Evaluation and Technical Support (FEATS) Contract (No. 68-C-00-185)
- Licking Valley School District generously allowed the use of its facilities for on-site testing since 2001
- Several adsorptive/oxidizing media manufacturers, distributors, and vendors provided samples
- Many Battelle staff provided field and laboratory support

Outlines

- Experimental design rationale
- Pilot-plant design and test conditions
- Results of As(V) adsorption tests
- Results of As(III) adsorption tests
- Conversion of As(III) to As(V)
- Observations and conclusions

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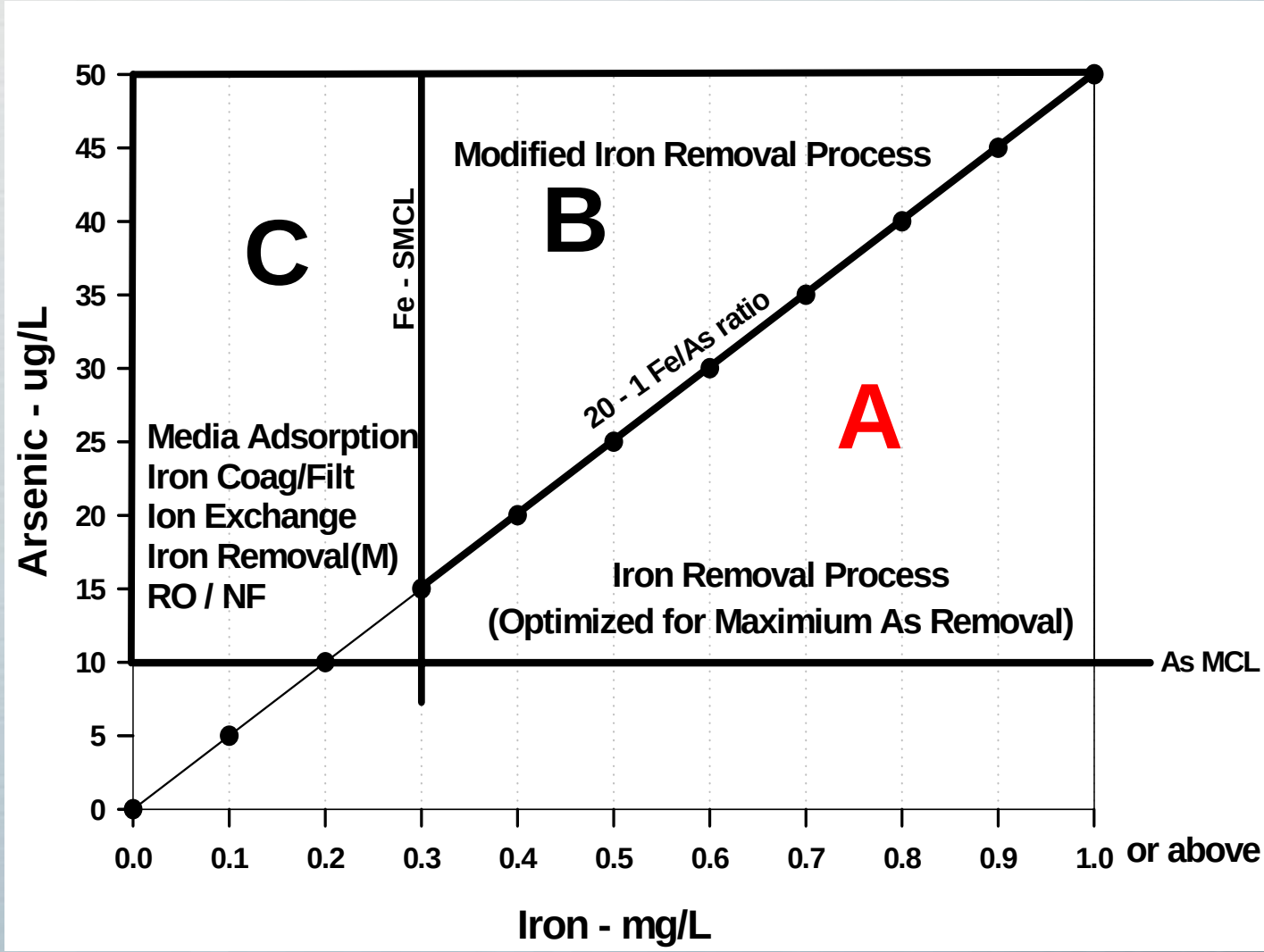
LVHS Water Quality

Analyte	Concentration Range
pH	7.7–8.0
Temperature (°C)	11.0–22.3
As_{total} (μg/L)	53–79
$As_{soluble}$ (μg/L)	56–73
$As_{particulate}$ (μg/L)	<0.1–16
As(V) (μg/L)	<0.1–13
As(III) (μg/L)	42–68
Fe_{total} (μg/L)	1,077–1,725
$Fe_{soluble}$ (μg/L)	795–1308
Mn_{total} (μg/L)	148–202
$Mn_{soluble}$ (μg/L)	146–185

Analyte	Concentration Range
Alkalinity (mg/L as $CaCO_3$)	200–245
Hardness (mg/L as $CaCO_3$)	165–187
NO_3-NO_2 (mg/L as N)	0.3
Silica (mg/L)	2.2
Sulfate (mg/L)	4.0
Sulfide (mg/L)	<1.0
Phosphate (mg/L)	<0.10–0.11
TOC (mg/L)	1.4
DO (mg/L)	1.0–1.7
ORP (mV)	-30-24

Technology Selection Chart



Experimental Approach

- As(V) adsorption tests
  - Pretreatment using solid oxidizing media to remove iron and Mn and convert As(III) to As(V)
- As(III) adsorption tests
  - No pretreatment
- Solid oxidizing media (SOM) tests

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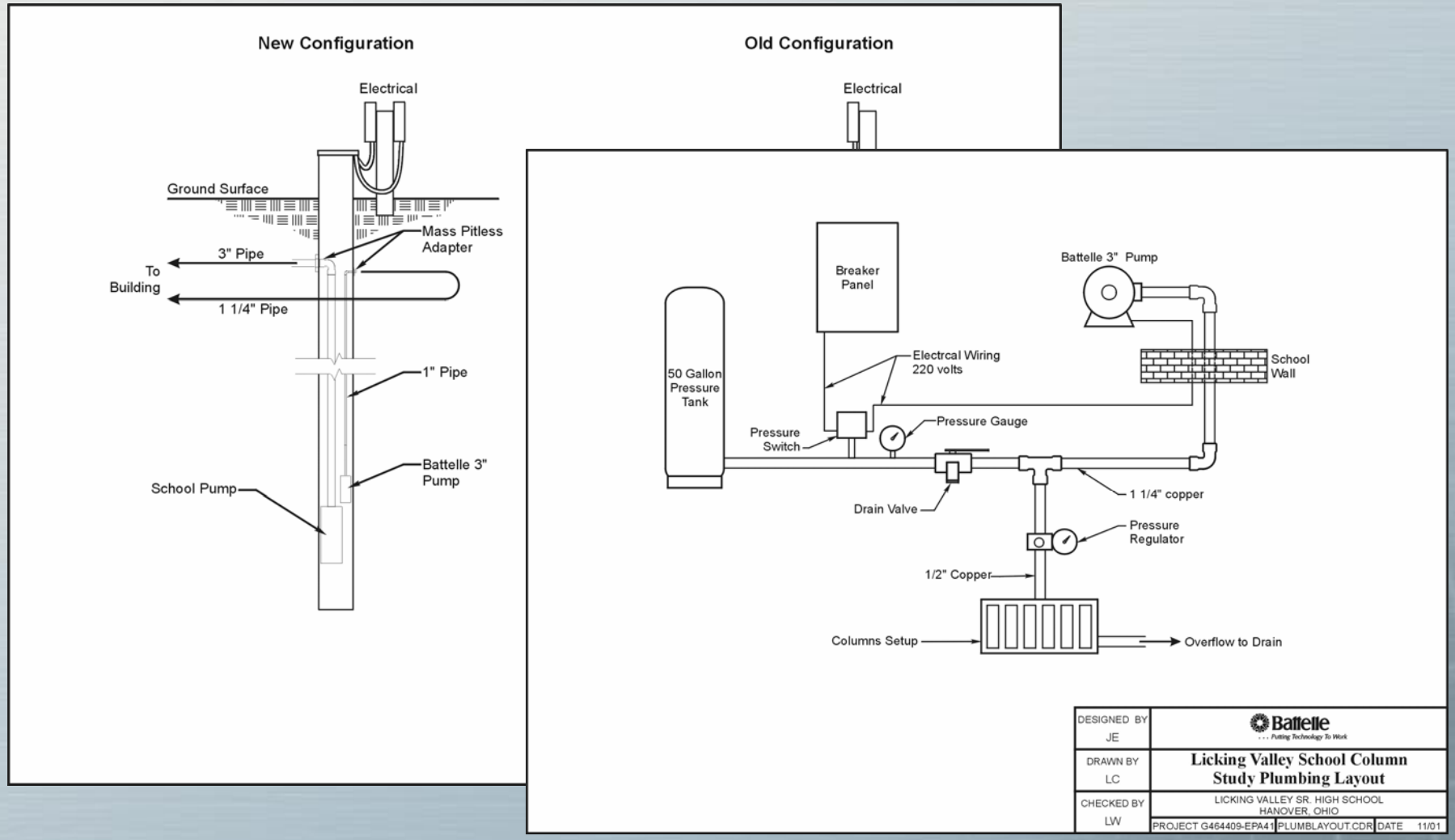
Pilot Study on Adsorptive Media

- Adsorptive media (13)
  - Alumina-based media (5)
    CPN; AAFS50; Aqua-Bind XP, MP; ARM100
  - Iron-based media (4)
    G2; E33; GFH; ARM200
  - Others (4)
    Titanium oxide-based media: MetSorb
    Nanoparticle selective resin: As:X^{np}
    Zeolite-based media: Zeocros B321
    F-400 GAC
- Solid oxidizing media (3)
  - Filox[a,b], Pyrolox[a], Brim

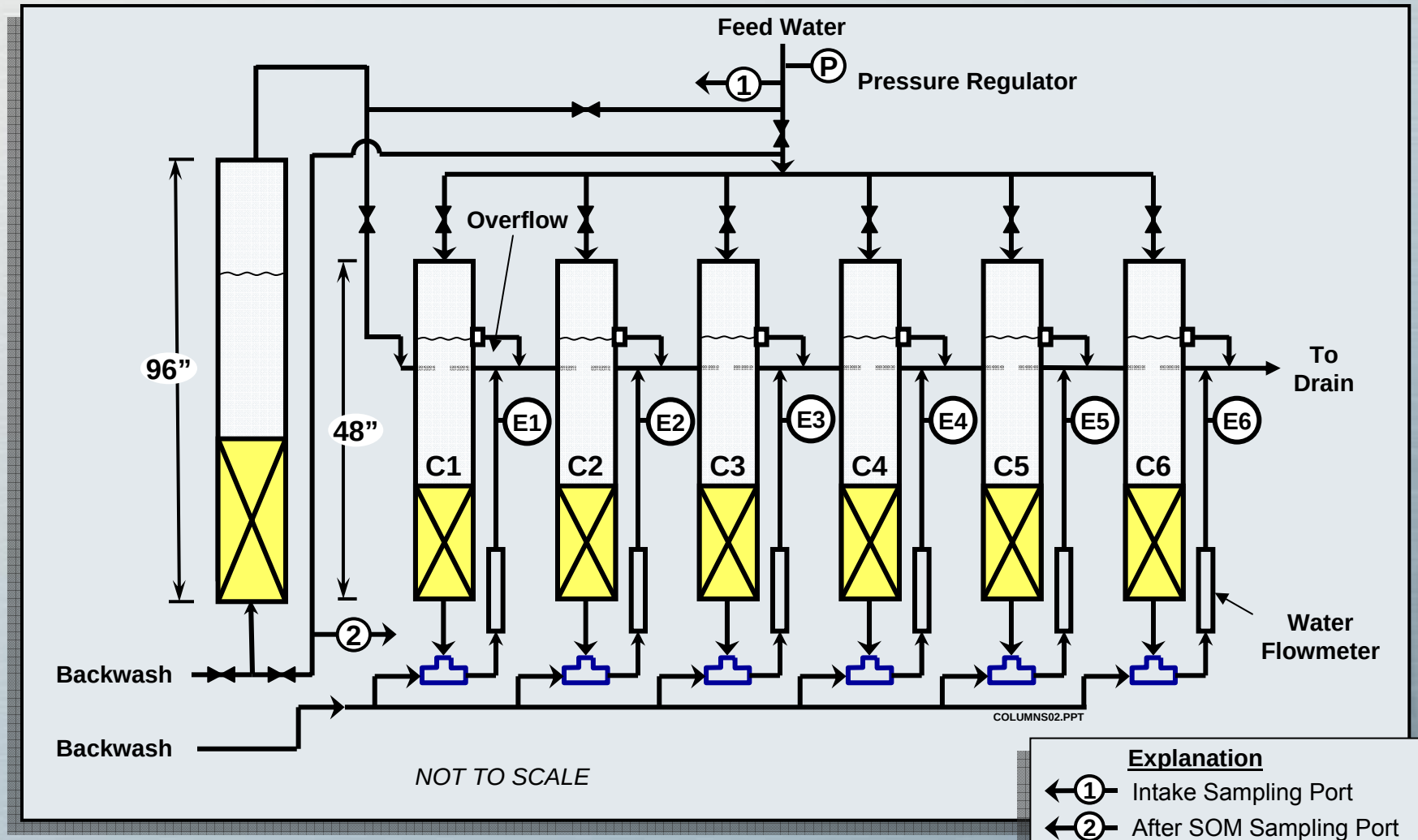
(a) Also known as Pyrolusite

(b) Currently branded as Metlease

Source Water Supply Schematic



Pilot-Plant Schematic



Explanation

- 1 — Intake Sampling Port
- 2 — After SOM Sampling Port
- E1 — Treated Water Sampling Ports
- Manual Valve

Properties of Alumina-Based Media

Parameter	CPN AA	AAFS50	Aqua Bind XP	Aqua Bind MP	ARM-100
Manufacturer	Alcoa	Alcan	Apyron	Apyron	Engelhard
Mesh size	28 × 48	28 × 48	28 × 48	28 × 48	18 × 50
Bulk Density, g/cm3 (lbs/ft3)	0.75 (47)	0.91 (57)	0.56-0.62 (35-39)	0.61-0.67 (38-42)	0.5 (32)
BET surface area ,m^2/g	300-340	200-250	190-230	190-250	200-260
Active ingredient	94.1% Al_2O_3	80-85% Al_2O_3 + proprietary additive	Alumina metal oxide composite	Alumina metal oxide composite	Alumina-based

Properties of Iron-Based Media

	G2	ARM-200	E33	GFH
Manufacturer	ADI	Engelhard	Bayer	USFilter
Mesh size	0.32 mm (Effective size)	40 × 80 (Mesh size)	10 × 35 (Mesh size)	0.32-2 mm (Effective size)
Bulk Density, g/cm^3 (lbs/ft^3)	0.75 (47)	0.72-0.80 (45-50)	0.45 (28)	1.22-1.29 (76-81)
BET surface area, m^2/g	27	NA	142	127
Active ingredient	Diatomaceous earth (Si-based) impregnated with a coating of ferric hydroxide	Iron-based	Iron oxide composite (90.1% FeOOH)	52-57% $Fe(OH)_3$ and β- FeOOH

Properties of other Adsorptive Media

Parameter	As:X^{np}	Metsorb	Zeocros B321	GAC
Manufacturer	Solmetex	HydroGlobe	Unknown	Calgon
Mesh size	0.3-0.6mm (Effective size)	NA	NA	12 X 40 (Mesh size)
Bulk Density, g/cm^3 (lbs/ft^3)	0.74-0.81 (45-50)	0.8 (50)	NA	0.53 (33)
BET surface area, m^2/g	NA	NA	NA	800
Active ingredient	Nano particle selective resin with iron oxide as a functional group	Titanium oxide	Zeolite based media	Activated carbon

NA = not available

Properties of Solid Oxidizing Media

Parameter	Filox-R ™	Pyrolox	Birm ®
Manufacturer	Matt-Son	American Minerals	Clack Corporation
Mesh size	12 × 40	8 × 20	9 × 35
Bulk Density, g/cm^3 (lbs/ft^3)	1.8 (114)	2.0 (125)	0.7–0.8 (44–50)
BET surface area, m^2/g	NA	NA	NA
Active ingredient	75–85% MnO_2	MnO_2	<0.01% MnO_2

NA = not available

Test Conditions - Adsorption Columns

- Conditions applied to both As(V) and As(III) tests
- Media wet loading to remove fines
- System operated under constant pressure at about 15 psi
- Bed dimension 2” diameter × 12” long
- Bed volume 620 mL
- Flowrate 125−135 mL/min
- EBCT 4.8 ± 0.2 min
- No pH adjustment
- No backwash for adsorptive beds

Test Conditions - Pretreatment column

- Test conditions applied to As(V) tests only
- Dual media Birm and Filox
- Bed dimension 6” diameter × 16” long (8” per SOM)
- Bed volume 3,700 mL × 2
- Flowrate 750−810 mL/min
- EBCT 4.8 ± 0.2 min per SOM
- Backwash twice a week

Sampling and Analysis

- Sampling/speciation weekly at inlet, after pretreatment (for As[V] tests only), and after each adsorption column
- Speciation for total and particulate As, As(V), and As(III); total and soluble Fe, Mn, and Al
- Metals analysis
  - EPA Method 200.8
  - Perkin Elmer Sciex Model 6000 ICP/MS equipped with a crossflow pneumatic nebulizer and an auto-sampler
  - Detection limits of 0.1, 30, 0.5, and 11 µg/L for As, Fe, Mn, and Al, respectively
- On-site analysis
  - pH, DO, ORP, and temperature using a WTW multi-340i meter

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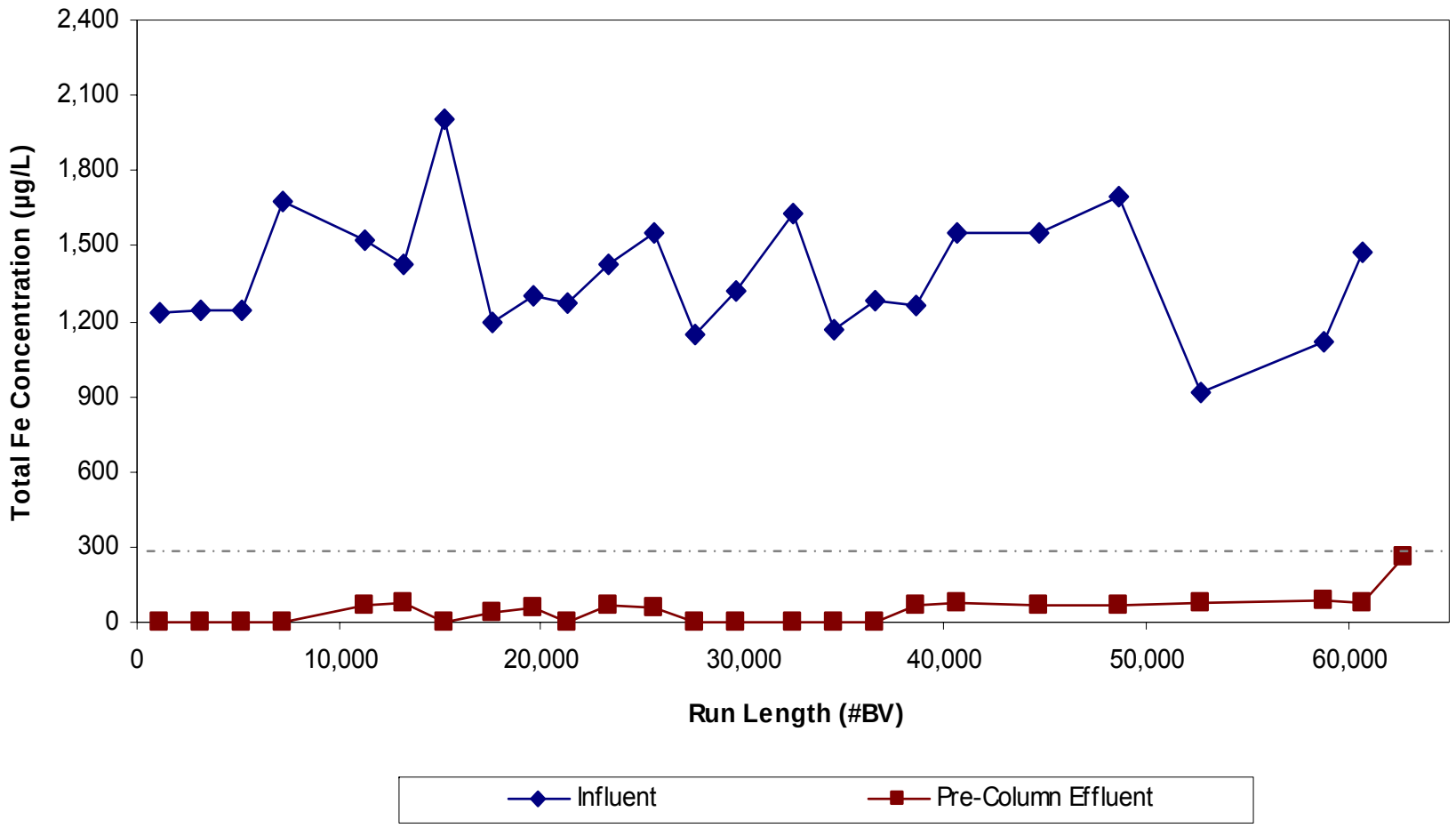
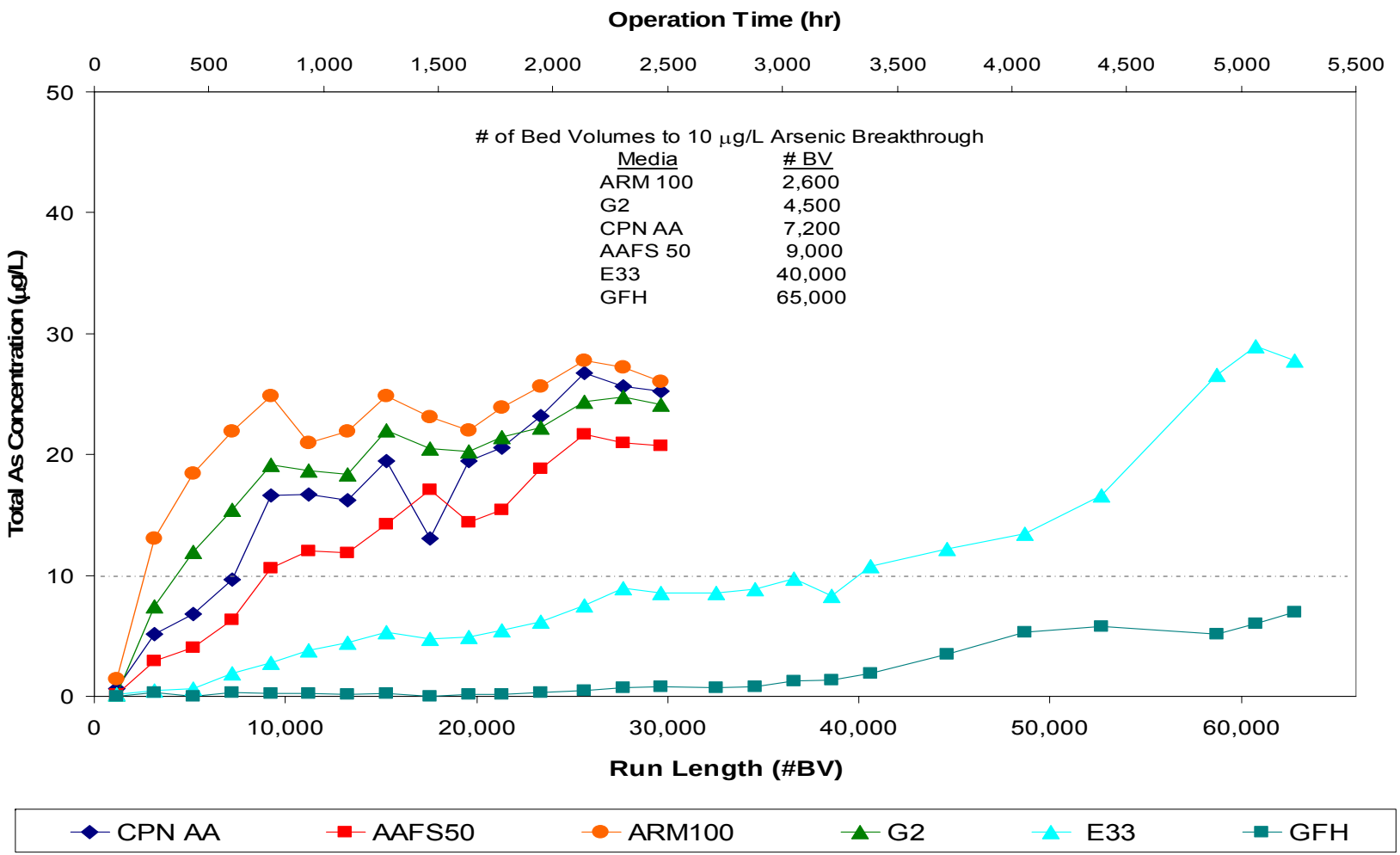
As(V) Test: Pretreatment - Arsenic

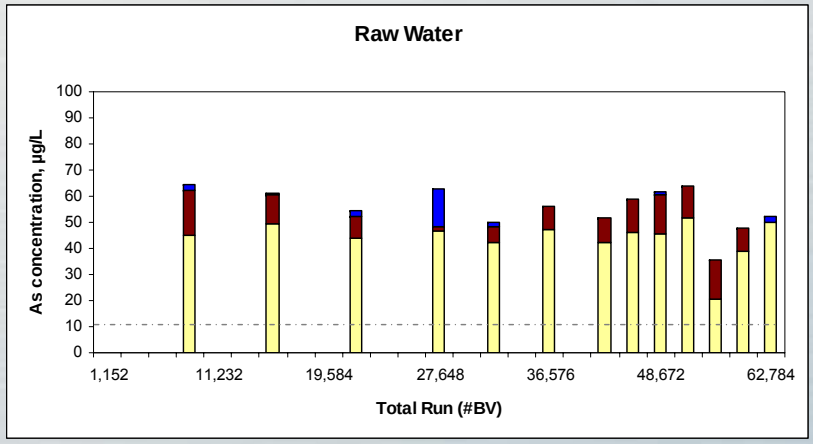
As(V) Tests: Pretreatment - Iron

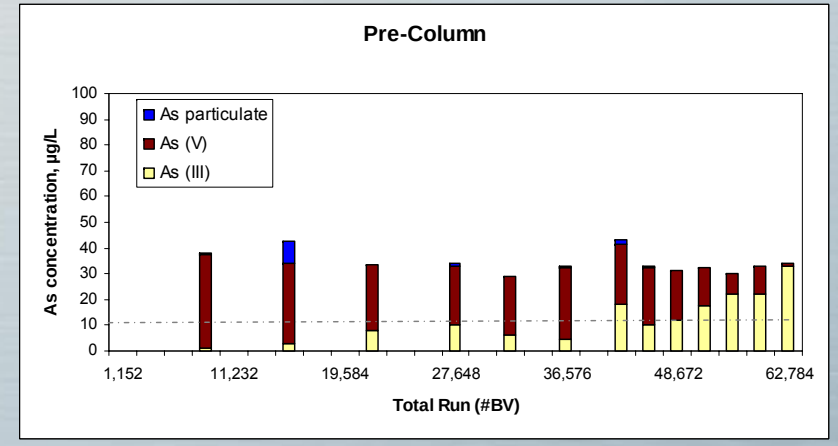


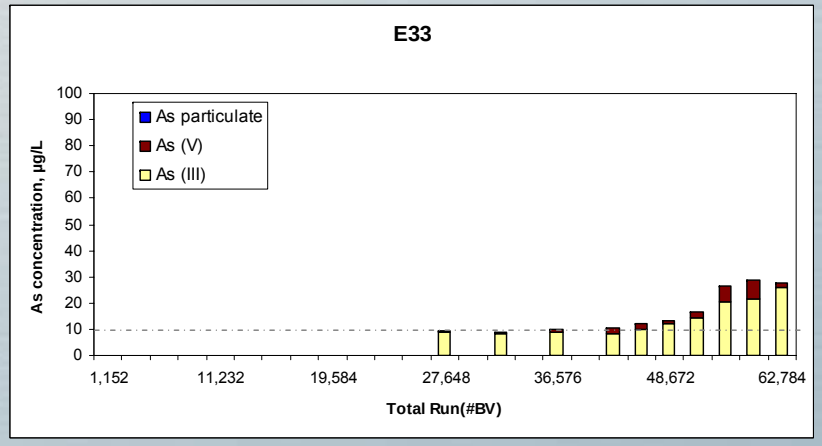
As(V) Tests: Breakthrough Curves

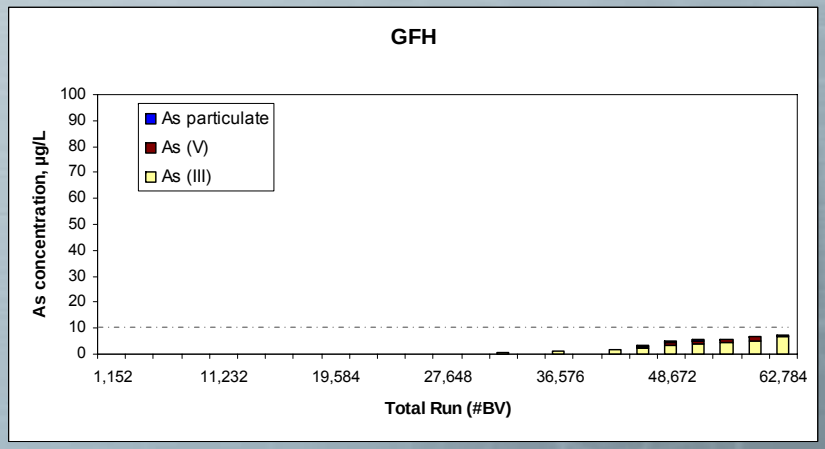


As(V) Tests: Speciation Results









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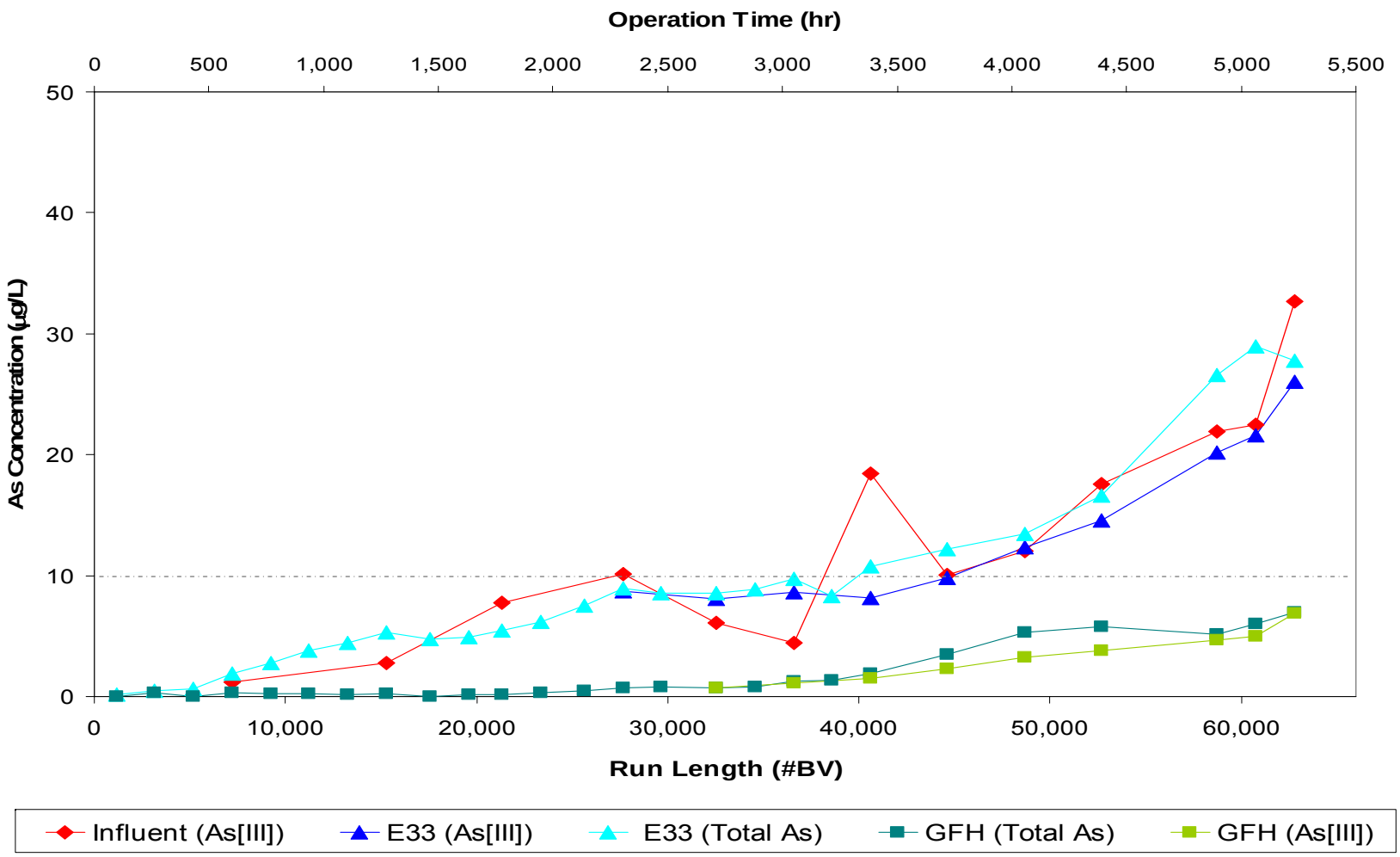
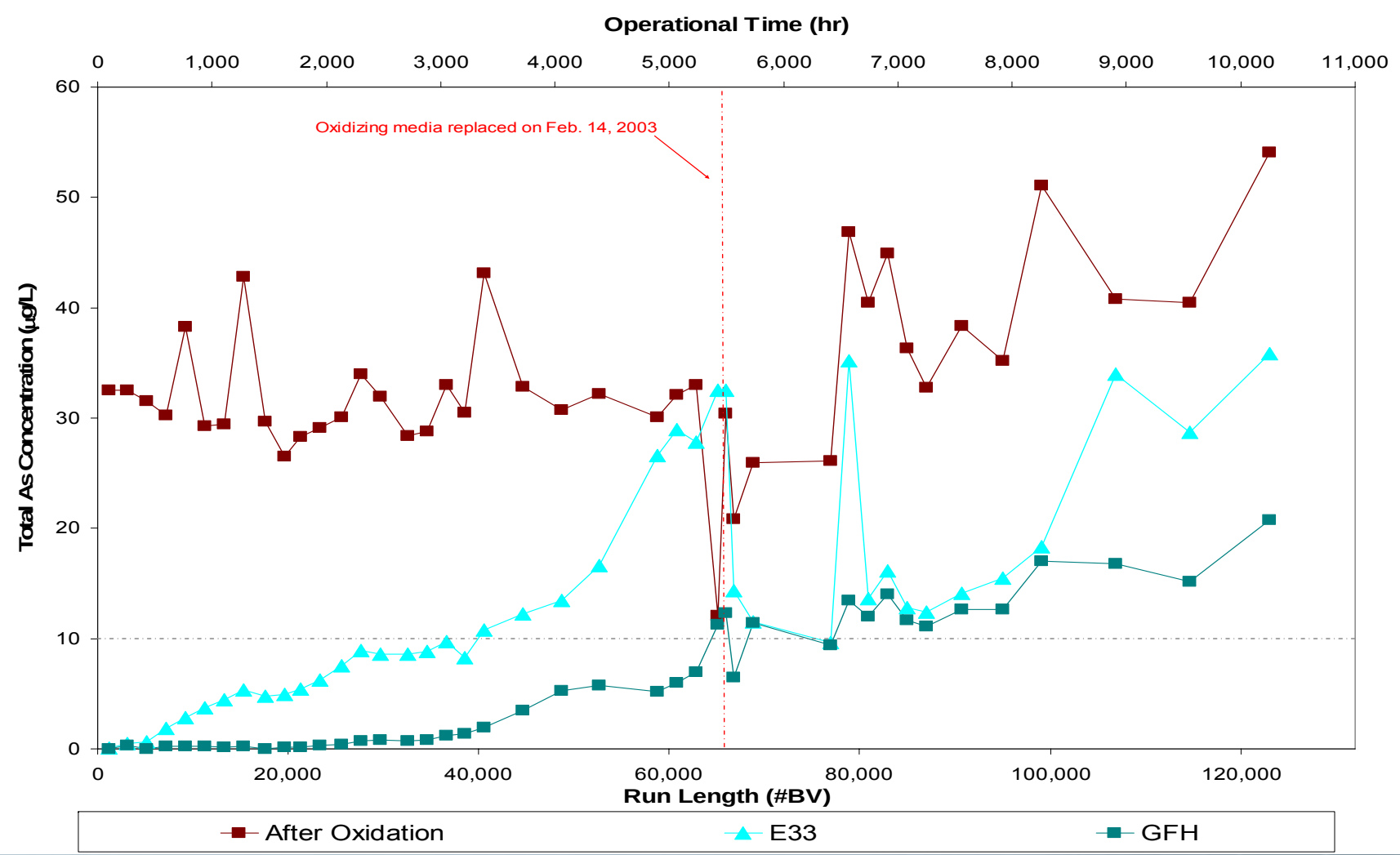
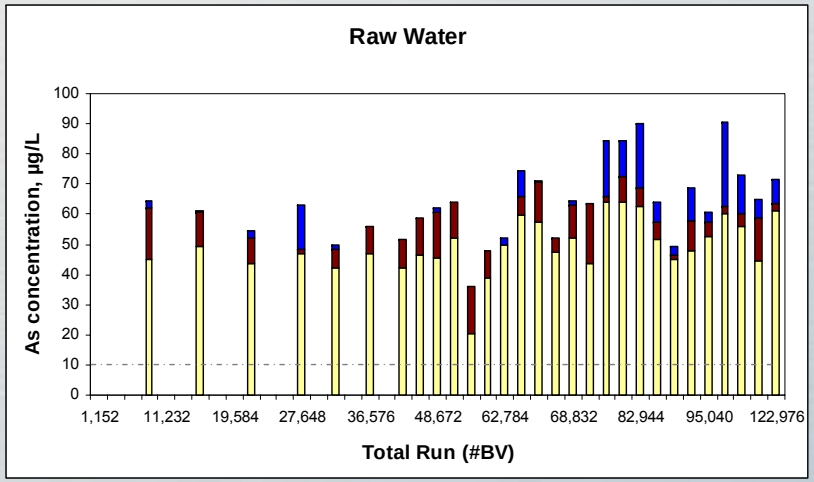
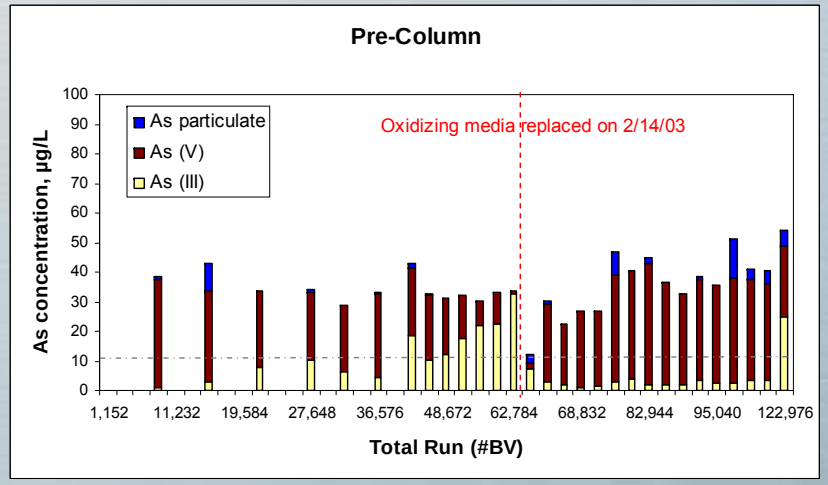


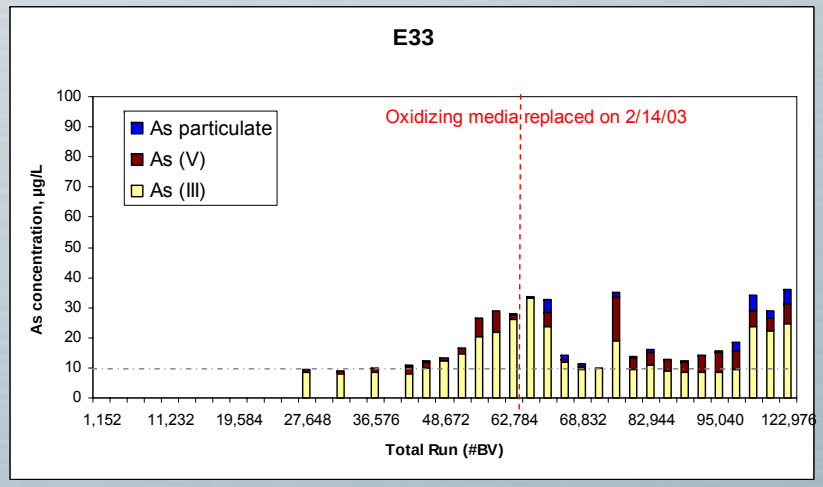
As(V) Tests: Breakthrough after SOM Re-bedding

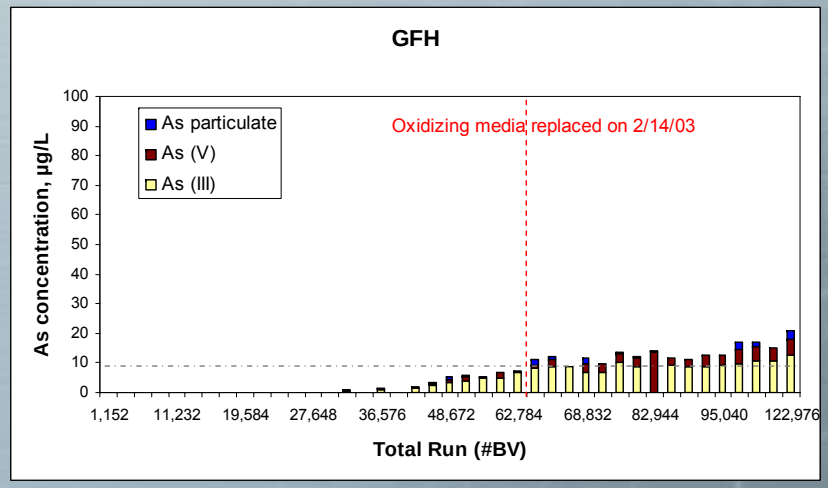


As(V) Tests: Speciation Results after SOM Re-bedding









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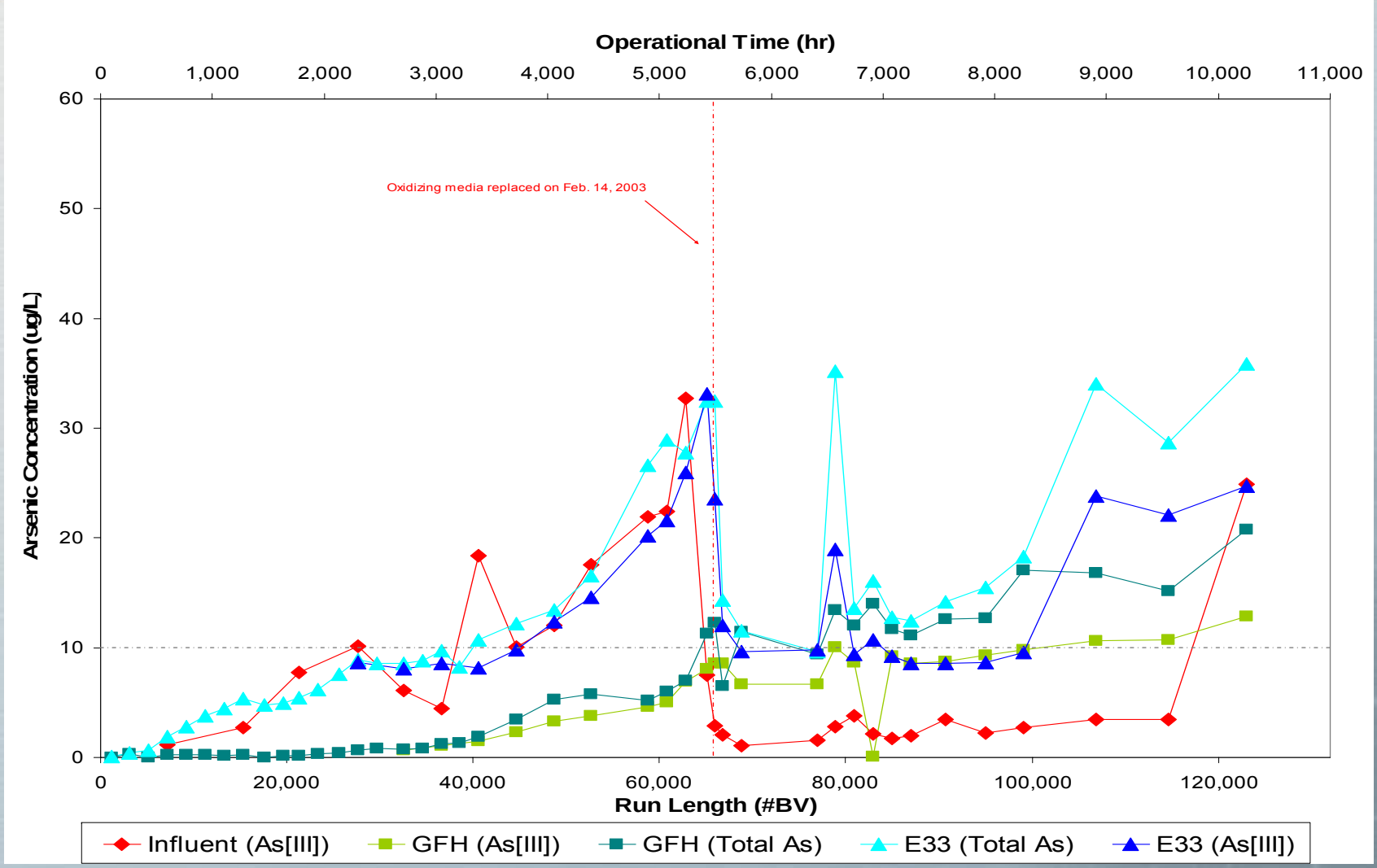

As(III) Mass Balance

Media	As(III) Entered during Run 1	As(III) Removed during Run 1	As(III) Removal (%)	As(III) in Treated Water during Run 2
E33	323	**54**	17	**155**
GFH	323	**296**	92	**101**

During Run 2:

- As(V) was the predominating species in the influent to both E33 and GFH
- As(III) was the predominating species in the GFH effluent, indicating displacement (???)
- The amount of As(III) in the E33 effluent was more than that removed by E33 during Run 1 – what does it mean?

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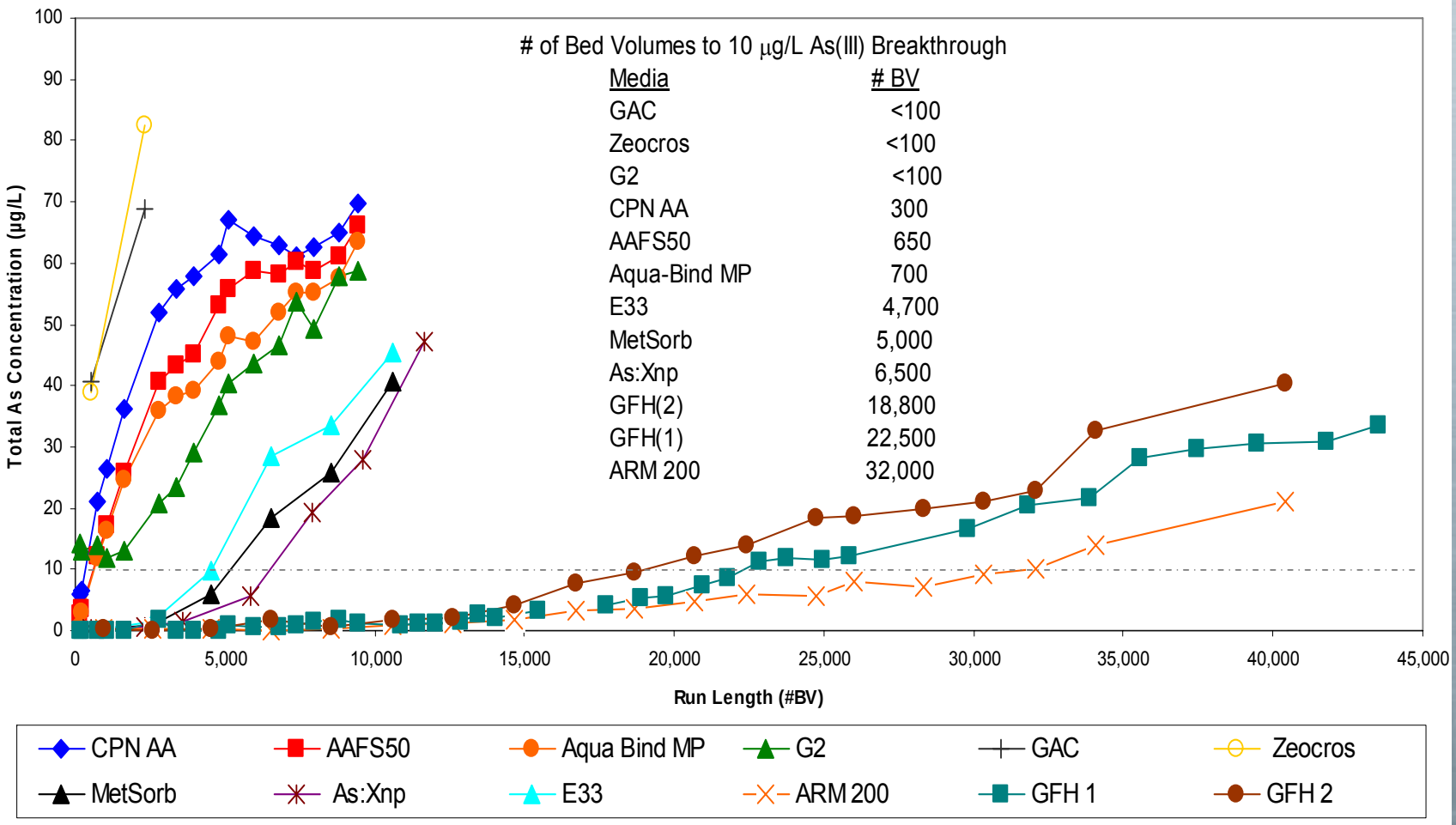
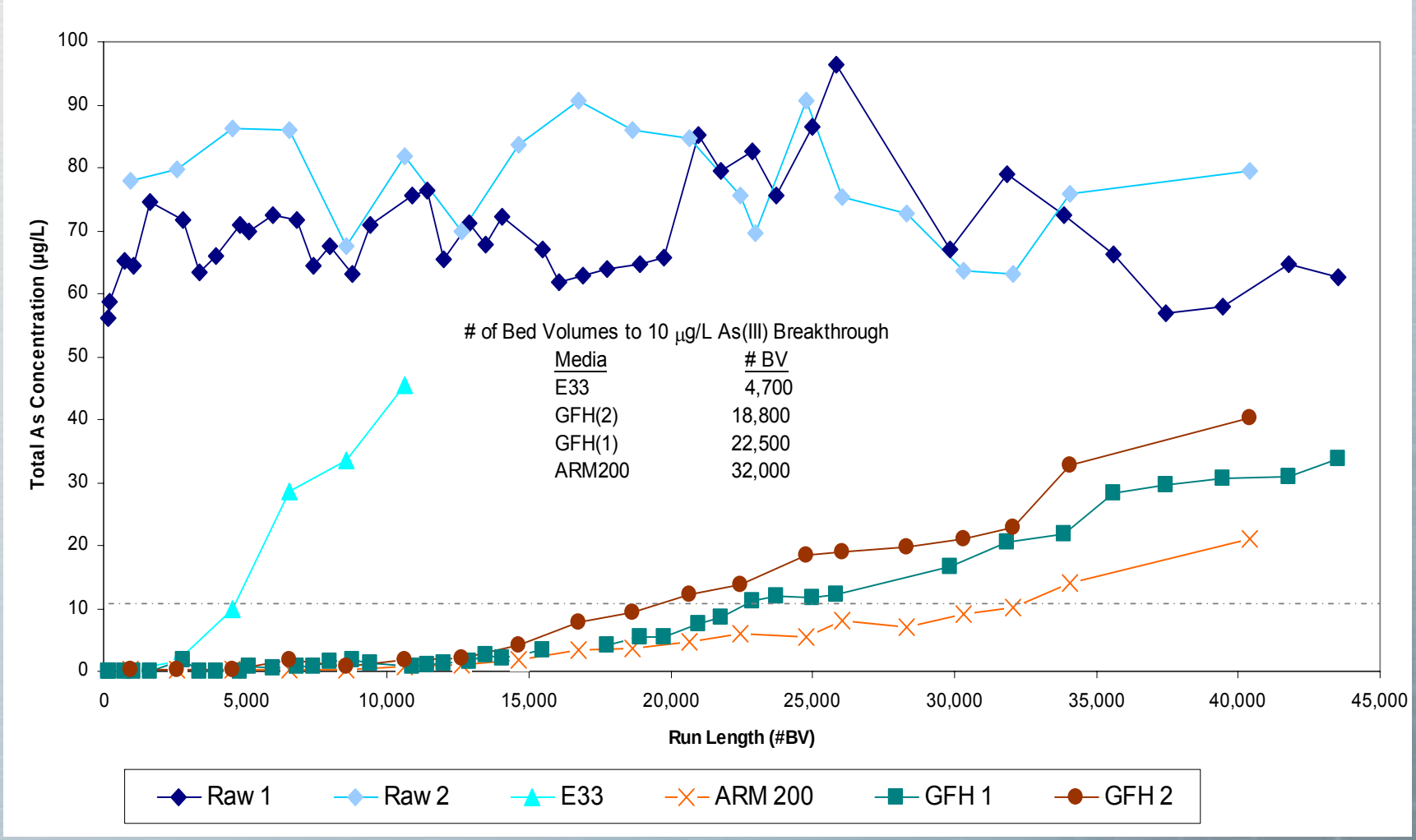
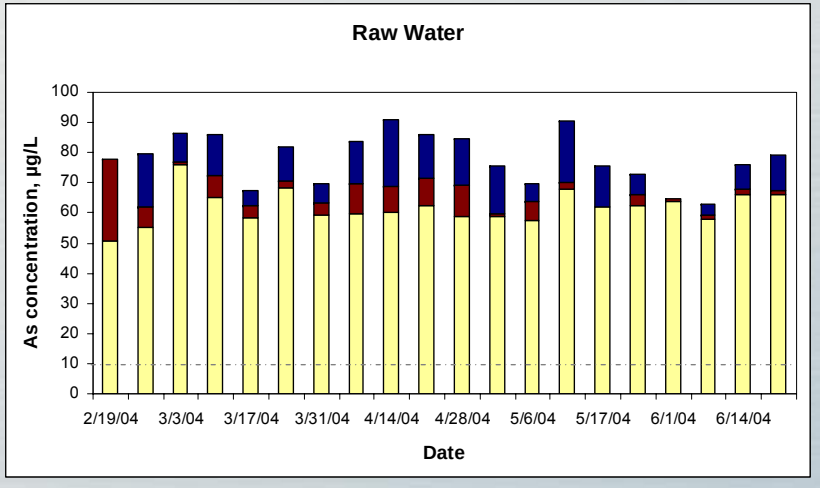
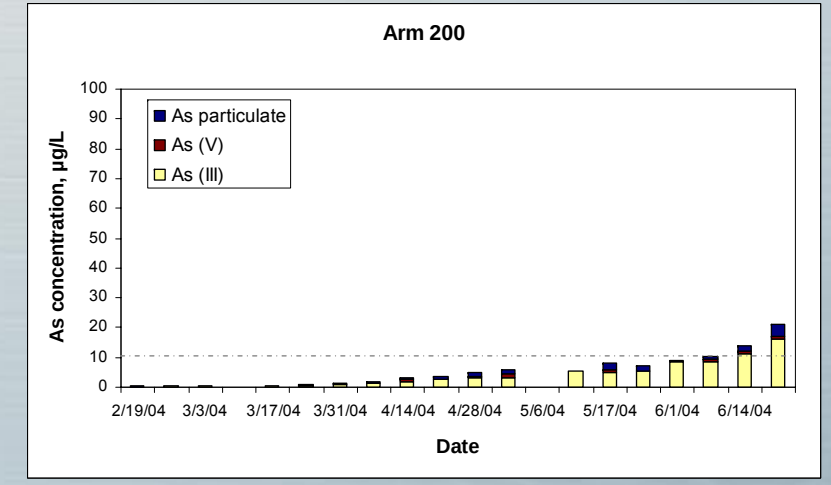


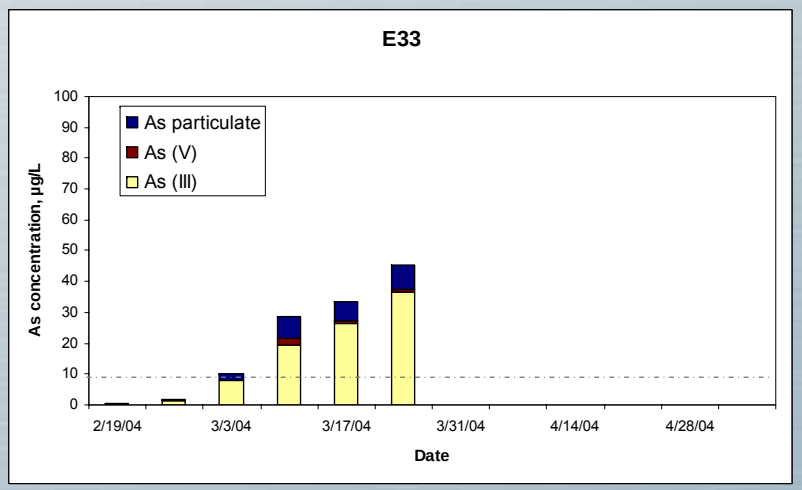
As(III) Tests: Breakthrough from E33, GFH and ARM 200

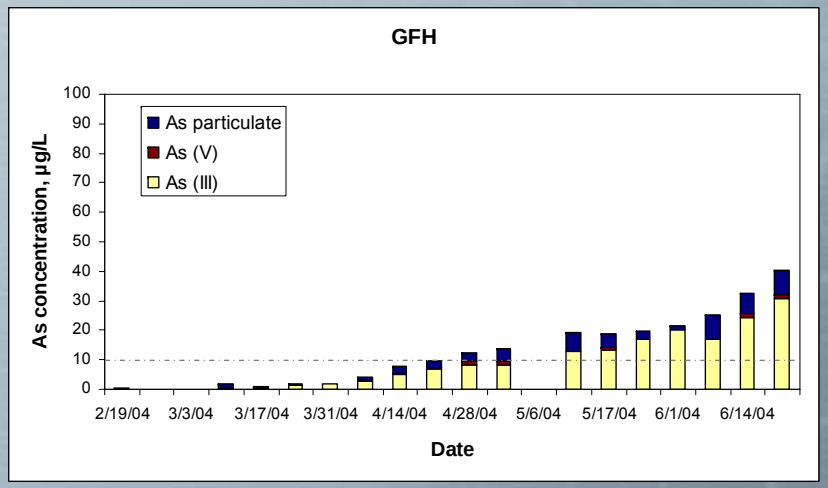


As(III) Tests: Speciation Results

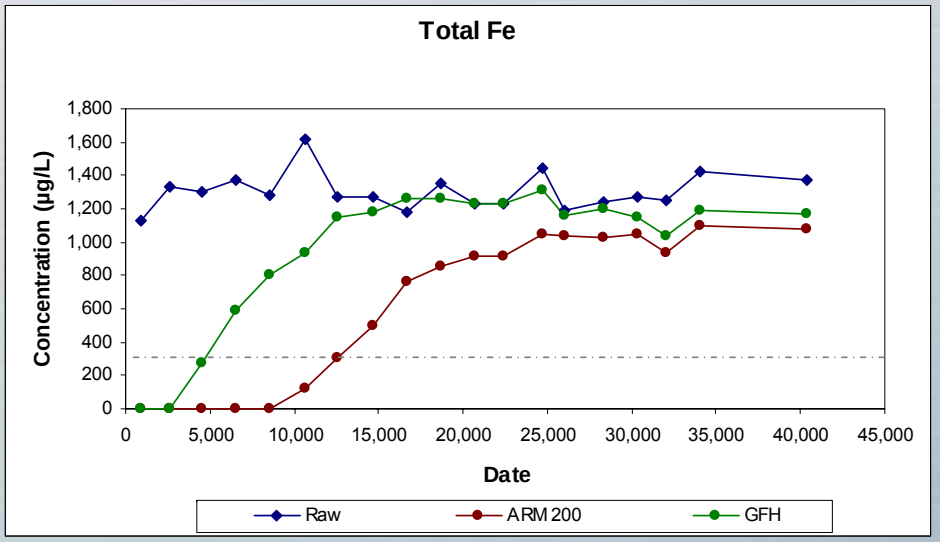


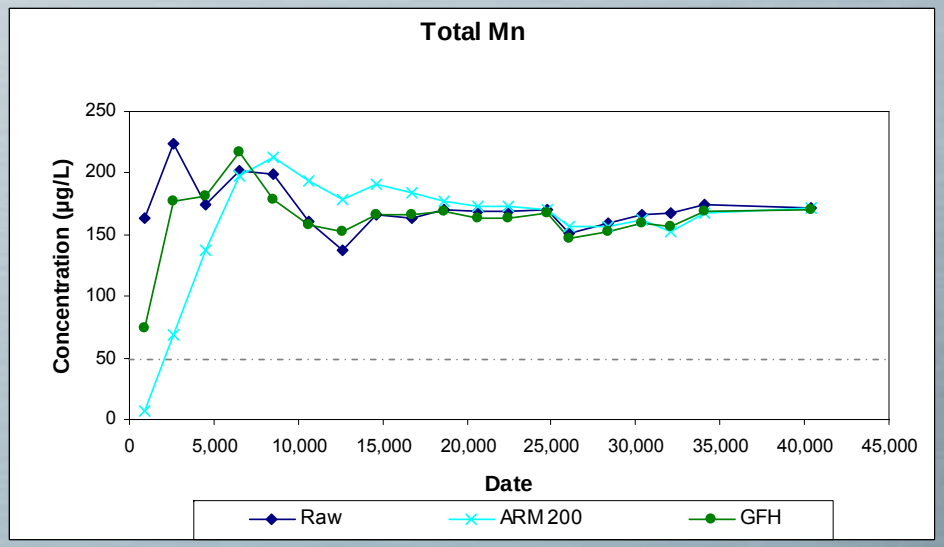






As(III) Tests: Fe and Mn Breakthrough





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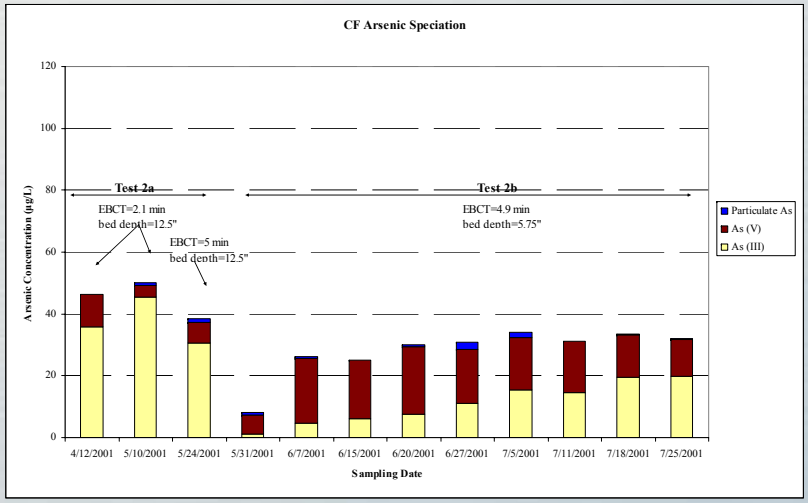
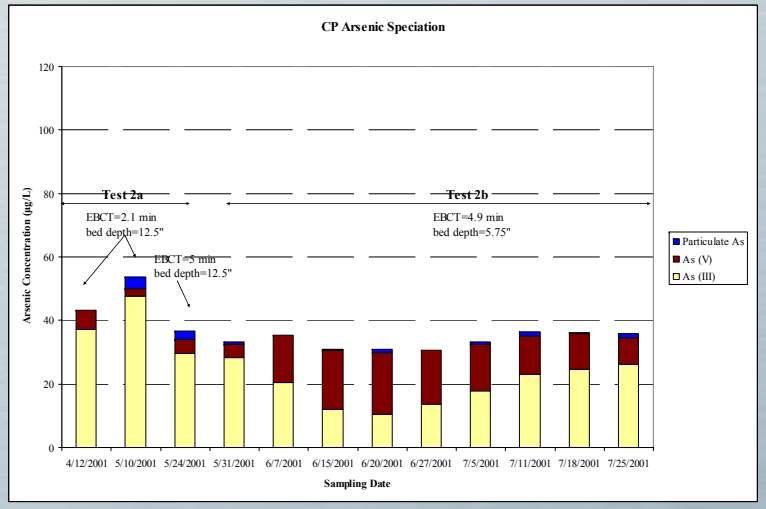
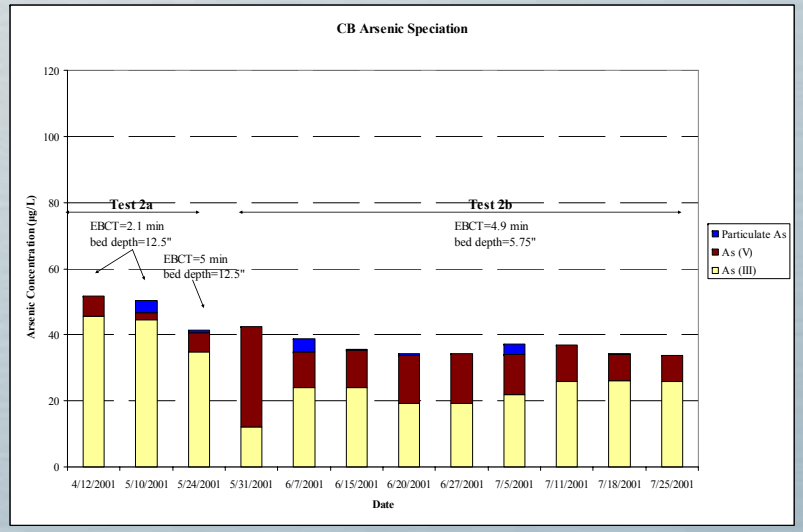
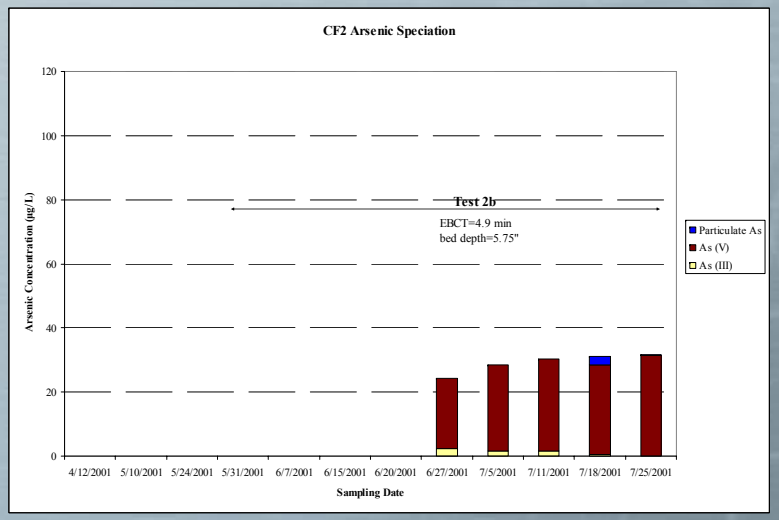
As Conversion with Filox or Birm/Filox









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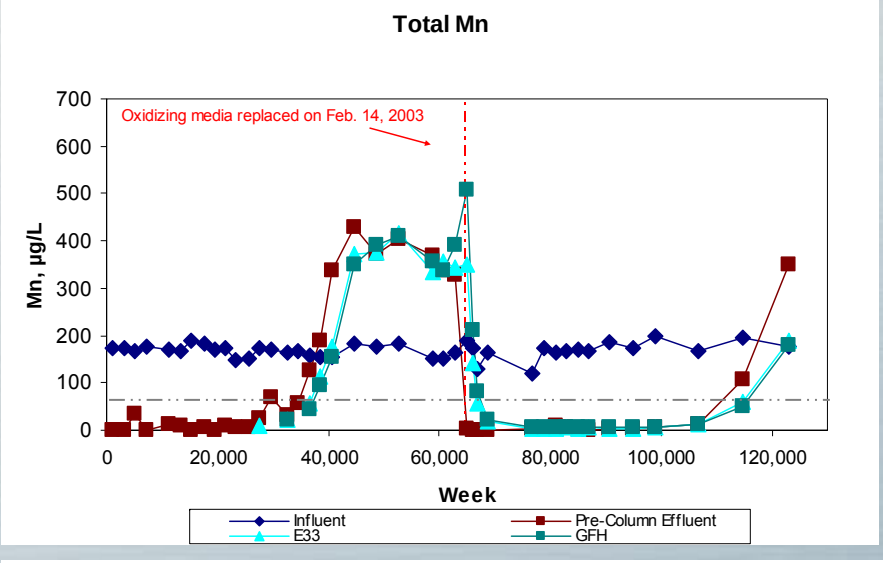
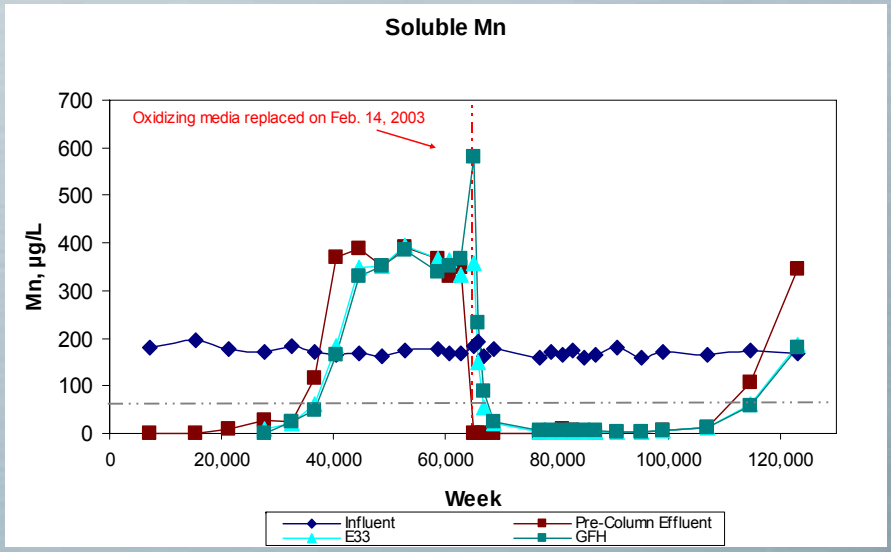
Observations and Conclusions

- In general, iron-based media outperformed Al-based media for arsenic removal with media life ranging from 2,000 to 9,000 BVs for Al-based media and 40,000 to 65,000 BVs for E33 and GFH.
- Adsorptive media had much higher capacities for As(V) than for As(III). However, ARM 200 and GFH had a long media life of 34,000 and 24,000 BVs for As(III), respectively.
- As(III) can be released from adsorptive media through displacement or surface-mediated conversion (?).
- Solid oxidizing media can be used as a pretreatment step before adsorptive media. Frequent backwash is essential to effectively remove Fe and/or convert As(III) to As(V).

As(V) Tests: Mn Leaching from Oxidizing Media