

In-Situ Flushing for DNAPL Source Mass Extraction

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Opening Comment

- In making DNAPL site remediation decisions, we have the option of defaulting to:
 - the certainty & comfort of mandated, prescriptive, conservative endpoints (e.g., MCL) that, in most cases, may not be technically achievable at a reasonable cost and within meaningful timelines,instead of considering as alternatives,
 - risk-based, technically achievable, cost-effective endpoints that allow some contamination to be left at the site, but with the obligation for long-term site stewardship, and might have significant public perception concerns, in spite of institutional and other controls.

In-situ Flushing: Technical Basis:

Legacy of Enhanced Oil Recovery Technologies

Addition of “modifiers” to injected fluids for enhanced solubilization, mobilization & desorption:

- Reduction in IFT (Total Trapping Number)
- Density modification for mobility control
 - modify DNAPL (e.g., Pennell et al., 2000, US Patent: 6,099,206)
 - modify groundwater (e.g., Miller, 2001; US Patents: 6,190,092: 6,261,029)
- Reduction in Viscosity (temp??)
- Reduction in wettability (of solid matrix or NAPL)
- Significantly increase desorption & mass transfer rate constants

Types of Source Zones

- **LNAPLs & DNAPLs**
 - **Fuel hydrocarbons (gasoline, diesel, kerosene, aviation fuels)**
 - **Transformer oils**
 - **Chlorinated & brominated solvents**
 - **Coal/oil tars**
 - **Creosotes**
- **Also used for sources with metals**

Complexity of Field Settings

– Size of Source Zone

- Small (e.g., dry cleaner & gasoline station): tens of m^3
- Intermediate (e.g., manufacturing sites): 100's m^3
- Large (e.g., disposal sites): 1000's m^3

– Hydrogeology

- Unconfined, mildly heterogeneous ($\sigma_{\ln \tau}^2 \sim 0.2$)
- Unconfined, moderately heterogeneous ($\sigma_{\ln \tau}^2 \sim 1$)
- Unconfined, highly heterogeneous ($\sigma_{\ln \tau}^2 \sim 2$)
- Fractured media & karst
- Sediments (streams, rivers, estuaries)???

τ is the “reactive travel time”

“Modifiers” Used

- Cosolvents (e.g., alcohols, ethyl lactate, ketones, ??)
- Surfactants (including food-grade)
- “Sugars” (e.g., cyclodextrins)
- “DOC” (e.g., “humics”)
- Organic acids & other “ligands” (for metals)
- Polymers (e.g., viscosity modifiers)
- Salts (injected fluid density modifiers)
- Foam-control additives & air (??)
- “Heat”??

Technology Status

- Extensive lab testing; scientific basis is well established
- Successful field testing for remediation of LNAPL & DNAPL sources in unconfined aquifers with mild to moderate heterogeneity (70-100% mass depletion reported)
- Simple & sophisticated numerical and “analytical” models available for scientific uses and site remediation design uses
- Several commercial applications, but not *yet* widely adopted at DNAPL sites

Examples of Recent Papers on In-Situ Flushing

- McGuire TM, McDade JM, Newell CJ 2006 Performance of DNAPL source depletion technologies at 59 chlorinated solvent-impacted sites GROUND WATER MONITORING AND REMEDIATION 26 (1): 73-84
- Oostrom M, Dane JH, Wietsma TW. 2006. A review of multi-dimensional, multi-fluid intermediate-scale experiments: Nonaqueous phase liquid dissolution and enhanced remediation VADOSE ZONE JOURNAL 5 (2): 570-598 MAY 2006
- Christ JA, Ramsburg CA, Abriola LM, Pennell KD, Loffler FE 2005 Coupling aggressive mass removal with microbial reductive dechlorination for remediation of DNAPL source zones: A review and assessment ENVIRONMENTAL HEALTH PERSPECTIVES 113 (4): 465-477
- Lee M, Kang H, Do W 2005 Application of nonionic surfactant-enhanced in situ flushing to a diesel contaminated site WATER RESEARCH 39 (1): 139-146
- Martel R, Foy S, Saumure L, et al. 2005. Polychlorinated biphenyl (PCB) recovery under a building with an in situ technology using micellar solutions, CANADIAN GEOTECHNICAL JOURNAL 42 (3): 932-948
- Saichek RE, Reddy KR. 2005. Electrokinetically enhanced remediation of hydrophobic organic compounds in soils: A review CRITICAL REVIEWS IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY 35 (2): 115-192
- Tick GR, Lourenso F, Wood AL, et al. 2005. Pilot-scale demonstration of cyclodextrin as a solubility-enhancement agent for remediation of a tetrachloroethene-contaminated aquifer ENVIRONMENTAL SCIENCE & TECHNOLOGY 37 (24): 5829-5834
- Schaerlaekens J, Feyen J 2004 Effect of scale and dimensionality on the surfactant-enhanced solubilization of a residual DNAPL contamination JOURNAL OF CONTAMINANT HYDROLOGY 71 (1-4): 283-306

In-Situ Flushing Case Studies* Generation-1 Technology?

2.0	<i>In Situ</i> Flushing Case Studies	5
2.1	Alameda Point Naval Air Station Site, Alameda, CA	5
2.2	Bachman Road Residential Wells Remediation Project, Ann Arbor, Michigan	6
2.3	Biosurfactant Flushing and Enhanced Remediation: <i>In Situ</i> Biostimulation Strategy for Intractable Shoreline Sediment Contaminated with Diesel Fuel, Australia	7
2.4	Boston Logan Airport Area, Boston, Massachusetts	8
2.5	Camp Lejeune Surfactant-Enhanced DNAPL Removal, Marine Corps Base Camp Lejeune, North Carolina	8
2.6	Dover AFB, Test Cell 3 Cosolvent Solubilization, Dover, Delaware	9
2.7	Sages, Jacksonville, Florida	10
2.8	Gulf Power, Lynn Haven, Florida	11
2.9	Hill AFB Operable Unit (OU) 2 Full-Scale Surfactant Flood, Layton, Utah	11
2.10	Howard University – The Use of Pervaporation and Ultrafiltration Membranes for the Separation, Recovery, and Reuse of Surfactant Solutions, Washington, DC	12
2.11	Ivey Environmental Services – Clark Oil Company, Fredericton, New Brunswick, Canada	13
2.12	Ivey Environmental Services – Commercial/Residential Site, Fredericton, New Brunswick, Canada	13
2.13	McClellan AFB – Surfactant/Cosolvent Enhanced Subsurface Remediation of DNAPLs, McClellan AFB, California	14
2.14	OK Tool Area at Savage Well Site, Hillsborough County, New Hampshire	15
2.15	Millican Field, Pearl Harbor, Hawaii	15
2.16	Strategic Environment Research and Development Program (SERDP) - Evaluation of Surfactants for the Enhancement of PCB Dechlorination in Soils and Sediments, Atlanta, Georgia	16
2.17	U.S. Department of Energy (DOE) Paducah Gaseous Diffusion Plant, Paducah, Kentucky	17

* Lauren Strbak, July 2000

http://clu-in.org/download/studentpapers/strbak_flushing.pdf

Why isn't In-Situ Flushing Used More at DNAPL sites?

- No champions in regulatory agencies
- Early concerns about injecting “modifiers” into aquifers for remediation
- Early design/implementation problems
- Misperceptions about "success"
- Misunderstandings about "cost"
- Concerns about "efficiency"
- Lack of large-scale applications @ DNAPL sites w/adequate performance monitoring
- Not enough "committed" technology vendors
- Gen-2 Innovations not yet used at many DNAPL sites?

Second Generation Surfactant Flushing*: Five Key Innovations

- **Well Placement and Screening**
- **Surfactant Formulation**
- **Pore Volumes Injected**
- **Manifolding of Injection & Extraction Wells**
- **Surfactant Disposal**

* Shiao et al., May 2006. Recent advances in surfactant-enhanced aquifer remediation: The Golden, OK case study. Battelle Conf., Monterey, CA.

DNAPL Source Remediation Goals*

EPA Groundwater Task Force, 2004

- **Site owners:** Cleanup to drinking water standards (e.g., MCLs) not realistic, but are rarely allowed to use alternative goals. Benefits of source mass depletion are outweighed by disadvantages.
- **Technology developers:** Significant mass depletion possible, but stringent cleanup goals inhibit technology use. Alternative performance goals are more relevant.
- **Site managers:** Alternative goals cannot be applied because source zone has not been reliably delineated from plume. No accepted performance measures to determine effectiveness. Concerns about uncertain reliability & long-term costs of alternative goals.

* <http://gwtf.cluin.gov>



Performance metrics included in evaluation:

• *Impact to DNAPL source:*

- Reductions in DNAPL mass
- Reductions in soil concentrations
- • Reductions in source zone lifespan

• *Impact to plume:*

- Reductions in concentrations
- Achievement of MCLs
- • Reduction in mass flux/discharge
- Changes in plume stability/growth

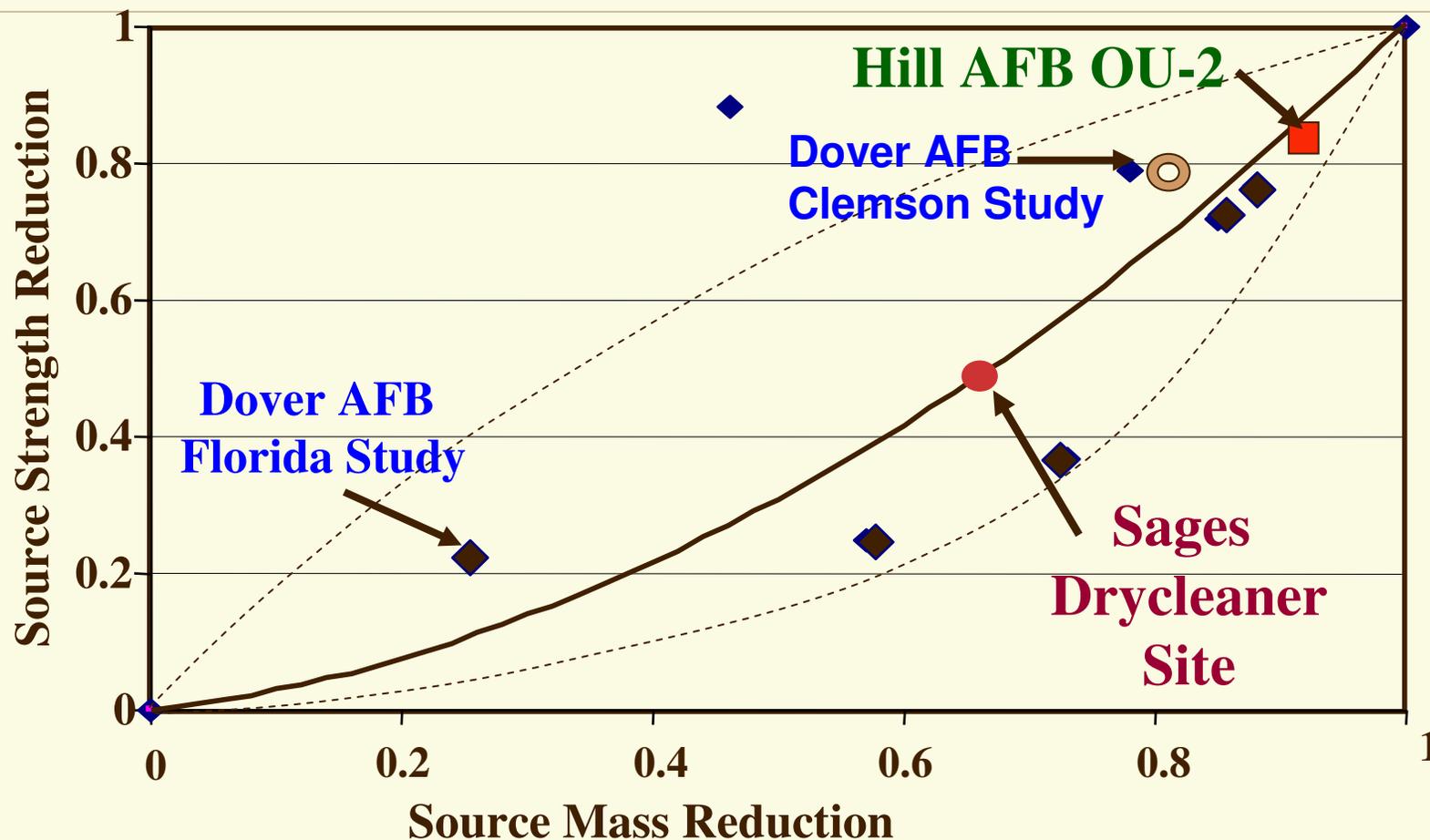
• *Adverse remedial impacts*

- DNAPL mobilization
- • Adverse changes in 2ndry gw quality
- Poor attenuation of toxic byproducts

• *Implementation considerations:*

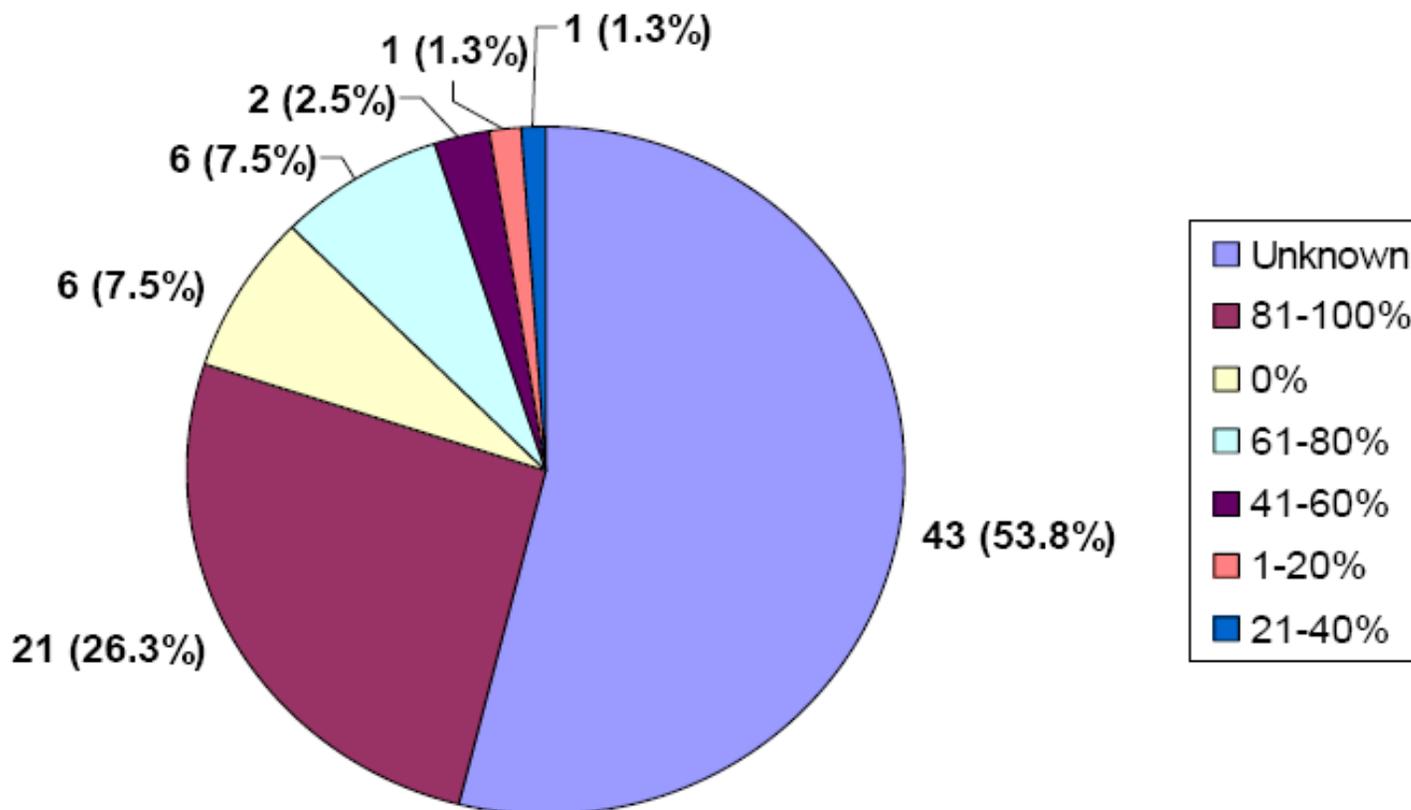
- Unit cost (volume/mass)
- Treatment duration
- • Occurrence of rebound
- Achievement of site closure

DNAPL Source Remediation: In-Situ Flushing Field Studies





Decrease in Mass Flux:



Total number of Sites with Mass Flux Data = 80

*From: [Assessing the Feasibility of DNAPL Source Remediation: Review of Case Studies](#).
 Naval Facilities Engineering Command, Contract Report (May 2004),
 CR-04-002-ENV. **Slide Courtesy of: Carmen Lebron, NFESC (2006)**

Performance of DNAPL Source Depletion Technologies*

- Data for 147 wells at 59 DNAPL source depletion sites were examined.
- Technologies included: Chemical Oxidation; Enhanced Bioremediation; Thermal Treatment; Surfactant/Cosolvent Flushing
- Criteria: CVOC conc.; rebound; treatment duration
- At 11 sites for which data were evaluated, *“concentration reduction for a given mass reduction was within 30% of the 1:1 relationship at most sites.”*
[Note: This implies $\Gamma \sim 1$, and source longevity large].
- However, MCLs were not achieved & sustained at all wells.

* McGuire, McCade, Newell, 2006. GWMR 26(1):73-84

In-Situ Flushing & Changes in Source & Flux Architecture*

- *The contaminant flux architecture at the source control plane (CP) is essentially invariant with time.*
- For DNAPL source zones cleaned up through in-situ flushing, areas with high contaminant fluxes remain high throughout the DNAPL mass depletion process.
- The contaminant flux distribution at the source CP gradually *fades away* with time.

*Details to be included in: Basu et al., 2006 (in preparation)

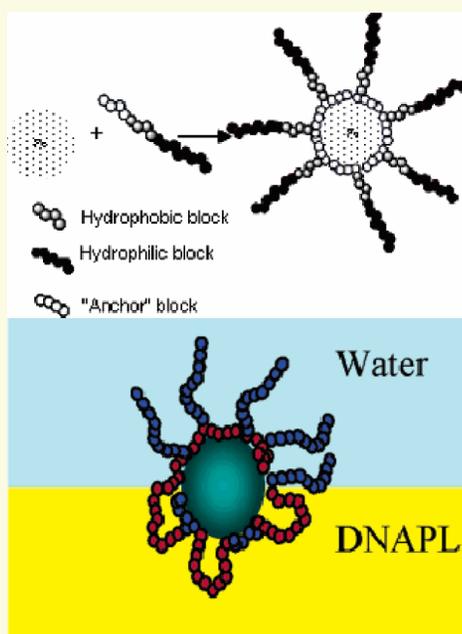
Technology Integration:

Combined Uses as “enhancers” with other technologies

- **Enhanced reduction**
 - Surfactants & cosolvents with ZVI (UF)
 - Emulsified ZVI (Reinhart et al., 2003, 2006; US Patents: 6,664,298; ?? (NASA))
- **Enhanced oxidation**
 - Permanganate (LFR Levine Fricke, 2005; US Patent 6,869,535; Purdue; Colorado School of Mines)
- **Enhanced Air Sparging (& SVE?)**
 - Kim et al.; UF: Purdue
- **Electro-kinetically Enhanced Flushing**
 - Reddy & Saichek (UIC)

Surfactant-Assisted Delivery of Nano-Iron Particles

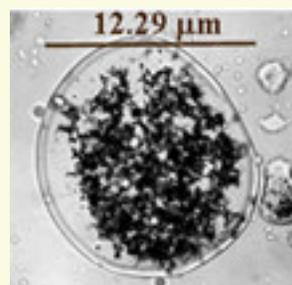
Targeting of the NAPL-water interface



Saleh et al. 2005 *Nano Let.*

Courtesy of: Andrew Ramsburg, Tufts Univ.

Encapsulations

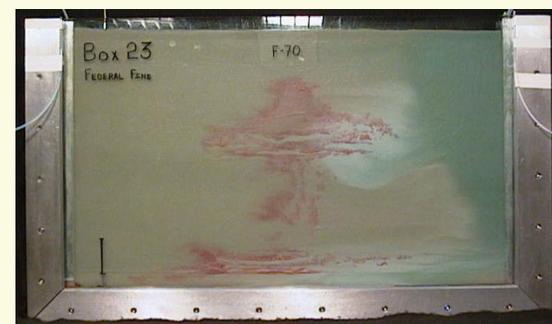


Quinn et al. 2005 *ES&T*



Allaire and Ramsburg, 2006
unpublished

Delivery & Influence on NAPL Architecture?



Ramsburg et al. 2004 *JCH*

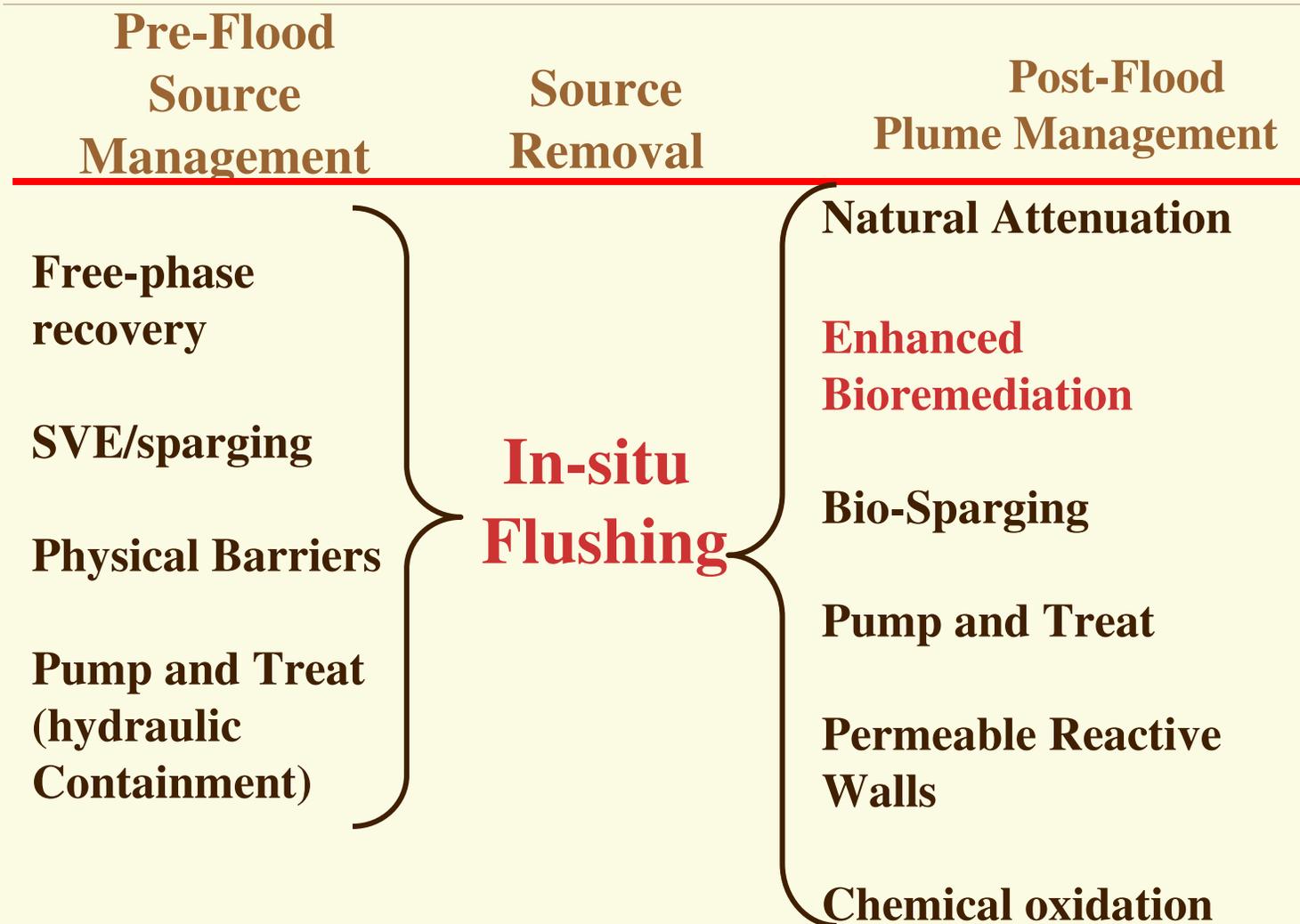
- Encapsulation of active ingredients has been demonstrated.
- Design must consider the stability of the NAPL architecture

Technology Integration:

Sequential Uses with other technologies
as “chasers” or “finishing” step

- Cosolvents/surfactants followed by reductive dechlorination (UF, Michigan, Hill OU2,?)
- Surfactants followed by low level chem. ox (Fenton) (B. Shiau, 2005, US Patent 6,913,419); Surbec LNAPL sites (e.g., Golden, OK)
- Thermal followed by low-level cosolvent/surfactant (primarily as e-donors)??
- Cosolvent/Surfactant flood followed by n-ZVI??
- ??

Integration of Remedial Technologies: Combinations, Sequencing & Optimization



Technology Implementation Challenges

- Concerns about “uncontrolled migration” & expansion of source zone
- “Incomplete” cleanup (Compliance/Closure)
 - Hydrodynamic Access
 - Sweep Efficiency
- Recovery/Reuse of “modifiers”
- Costs & Competitiveness
 - Net Present Value
 - Cost-to-Complete
- Scale – Which “niche” markets?

Research Needs

- Defining DNAPL source treatment goals by linking to benefits derived in the plume zone:
 - How much source mass should be depleted to achieve target source strength? (Mass reduction & Flux reduction relationships; what is Γ value? Initial mass?)
 - Where should mass depletion be targeted? Is cleanup of “hotspots” sufficient? (Source & flux architecture changes with remediation)
 - What is the role of mass *not* depleted (diffusive fluxes from low-permeability zones)?
 - What is the required e-donor flux to *enhance & sustain* plume attenuation?
 - Importance of increased total VOC flux??

Research Needs

- Secondary effects
 - Concerns about eco-toxicology
 - Changes in microbial diversity & functions
 - Increased BOD effects
 - Concerns about human-health effects
 - Safety issues (flammable?)
 - Mobilization of metals (e.g., Fe, Mn under reducing conditions induced by e-donor addition)
 - Human-health effects of modifiers