A Low-Cost Chemical Remediation Technology for Heavy Metals in Shipyard Stormwater

SBIR Topic N06-133

SIROM Scientific Solutions

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SIROM TECHNOLOGY

- SIROM has developed a new generation of low cost and highly efficient adsorbents.
- “Green” technology designed to remove heavy metals and other contaminants from aqueous streams.
- SIROM Adsorbents can be incorporated in standard treatment units such as packed bed filters, continuous and batch reactors depending on the objectives and treatment constraints.

SIROM Adsorbents

- Raw material is by-product of drinking water treatment.
- Primarily amorphous masses of aluminum and iron hydroxides
- Contain sediment and humic substances removed from raw water, as well as activated carbon and polymers added to raw water.
- More than 2 million tons generated each year in US.

SIROM Adsorbents

	pH	% Solids	Total						Oxalate (200 mM)	
			C	N	P	Al	Fe	As	Al	Fe
			----------$g \cdot kg^{-1}$----------							
SIROM A	**5.6**	**80.5 ±2.7**	**188.0 ±0.5**	**4.5 ±0.3**	**3.2 ±0.5**	**87.1 ±16.0**	**4.6 ±0.1**	**0.015 ±0.002**	**82.3 ±1.9**	**4.1 ±0.2**
SIROM F	**6.0**	**77.5 ±0.1**	**196 ±0.1**	**7.8 ±0.1**	**2.7 ±0.2**	**1.3 ±0.1**	**170.0 ±13.6**	**0.013 ±0.004**	**0.36 ±0.01**	**78.6 ±8.0**

Toxicity Characteristic Leaching Results for SIROM Sorbents (in $mg \cdot kg^{-1}$)

	As	Cd	Cr	Cu	Pb	Hg	Ni	Se	Zn
	$mg \cdot kg^{-1}$								
SIROM A	<0.506	<0.166	<0.168	<0.936	<1.092	11.0	<1.62	15.0	<0.054
SIROM F	<0.506	<0.166	<0.168	<0.936	<1.092	10.8	<1.62	13.4	<0.054
EPA limit	75	89	3000	4300	840	57	420	100	7500

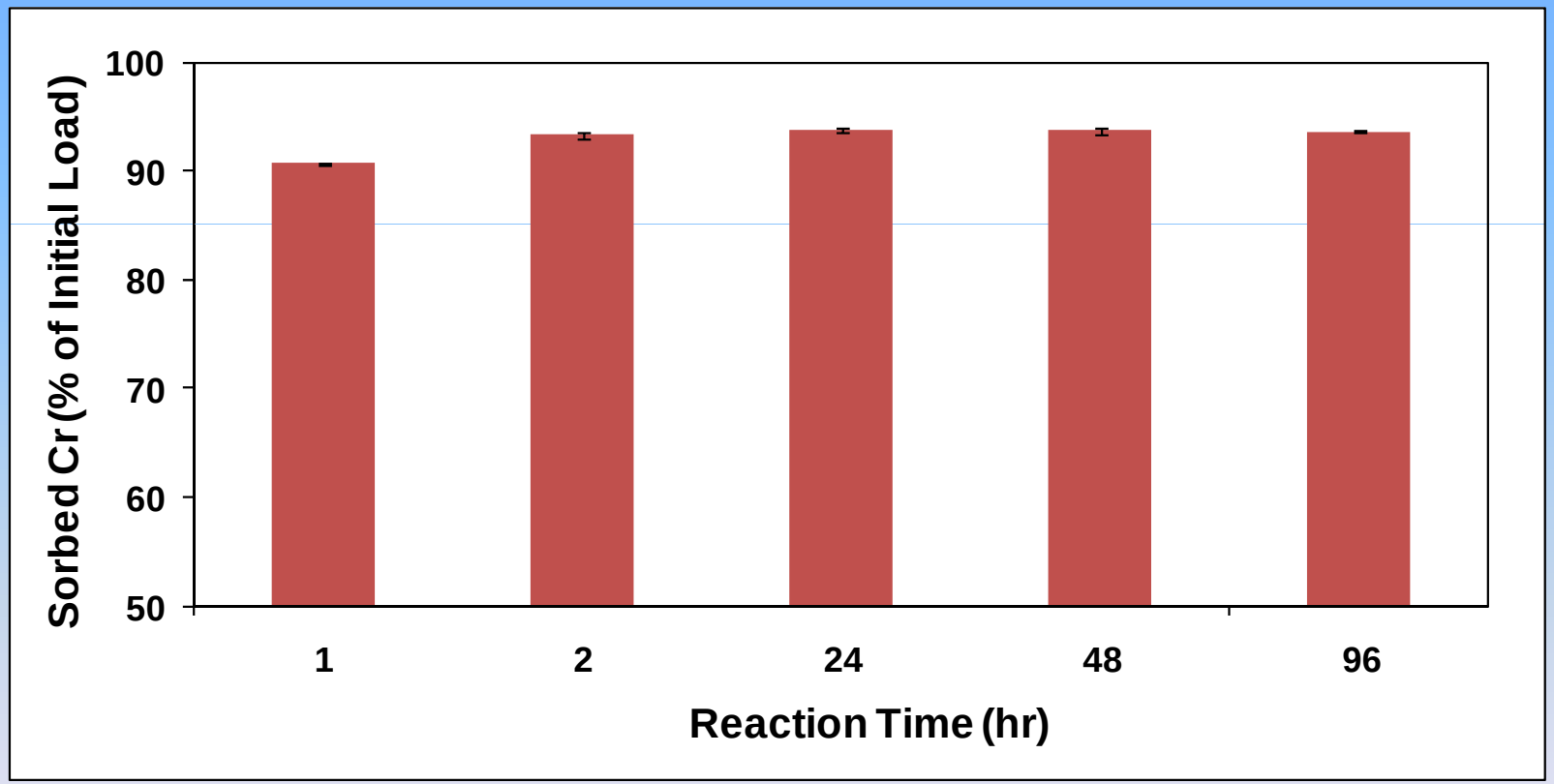
- TCLP results indicate that the spent SIROM Sorbents are classified as non-Hazardous wastes

SIROM Advantage

Comparison with Other Approaches			
		Chemical	SIROM
	Sedimentation	Precipitation	Solution
Chromium Removal	High	Very High	Very High
Copper, Lead Removal	Low	Very High	Very High
Zinc Removal	Low	Very High	High
Waste Disposal	Yes	Yes	Yes
Cost	Low	High	Low
Scalability	High	Medium	High
Portability	NO	YES	YES

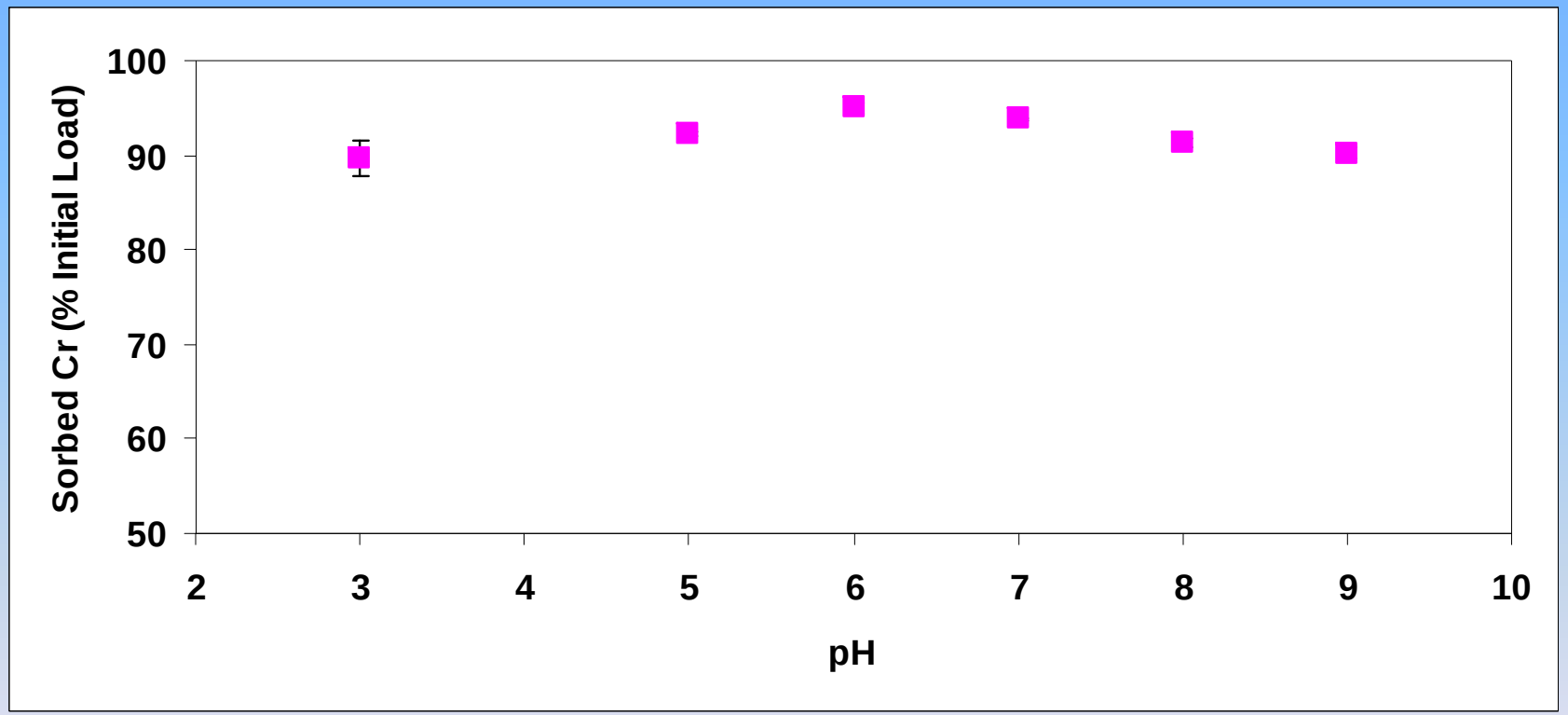
Phase I Results

Cr(VI) Adsorption in Standard Solutions



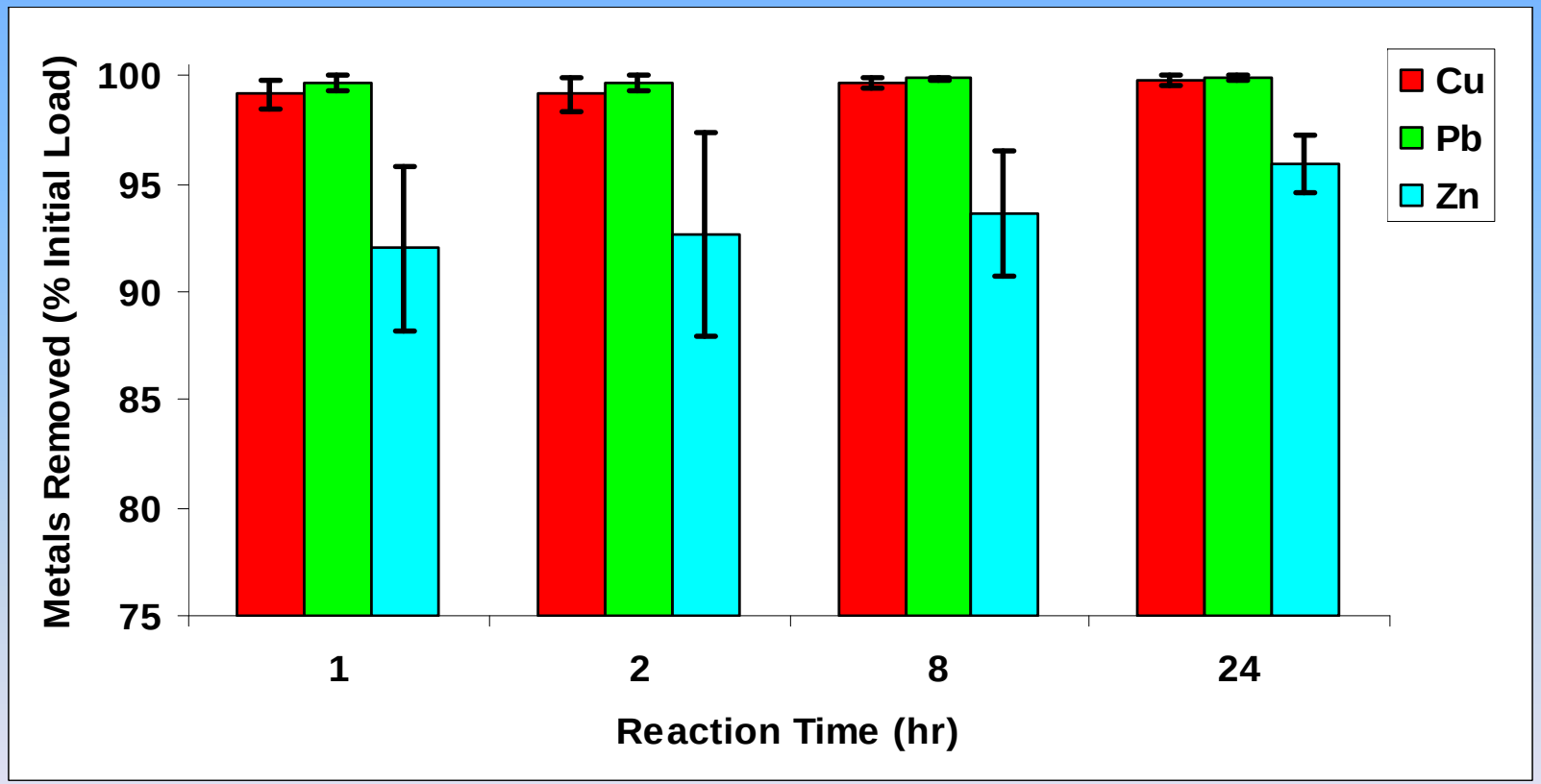
Cr(VI) sorption kinetics by SIROM A from standard Cr(VI) solutions. Solid to solution ratio was 1:5 (g SIROM A: mL solution). Initial chromium load was 500 mg kg^{-1}. Data are expressed as the mean (n=2) ± one standard deviation.

Effect of pH on Cr(VI) Adsorption



Effect of pH on Cr(VI) sorption kinetics by SIROM A. Solid to solution ratio was 1:5 (g SIROM A: mL solution) in synthetic shipyard stormwater. Reaction time was 24 hours and initial chromium load was 500 mg kg^{-1}. Data are expressed as the mean (n=2) ± one standard deviation.

Metals Adsorption in Standard Solutions (SIROM-A)



Metals sorption kinetics by the SIROM-A from standard solutions. Solid to solution ratio was 1:5 (g SIROM: mL solution). Initial metal load was 2500 mg kg^{-1} for copper, lead, and zinc. Data are expressed as the mean (n=3) ± one standard deviation.

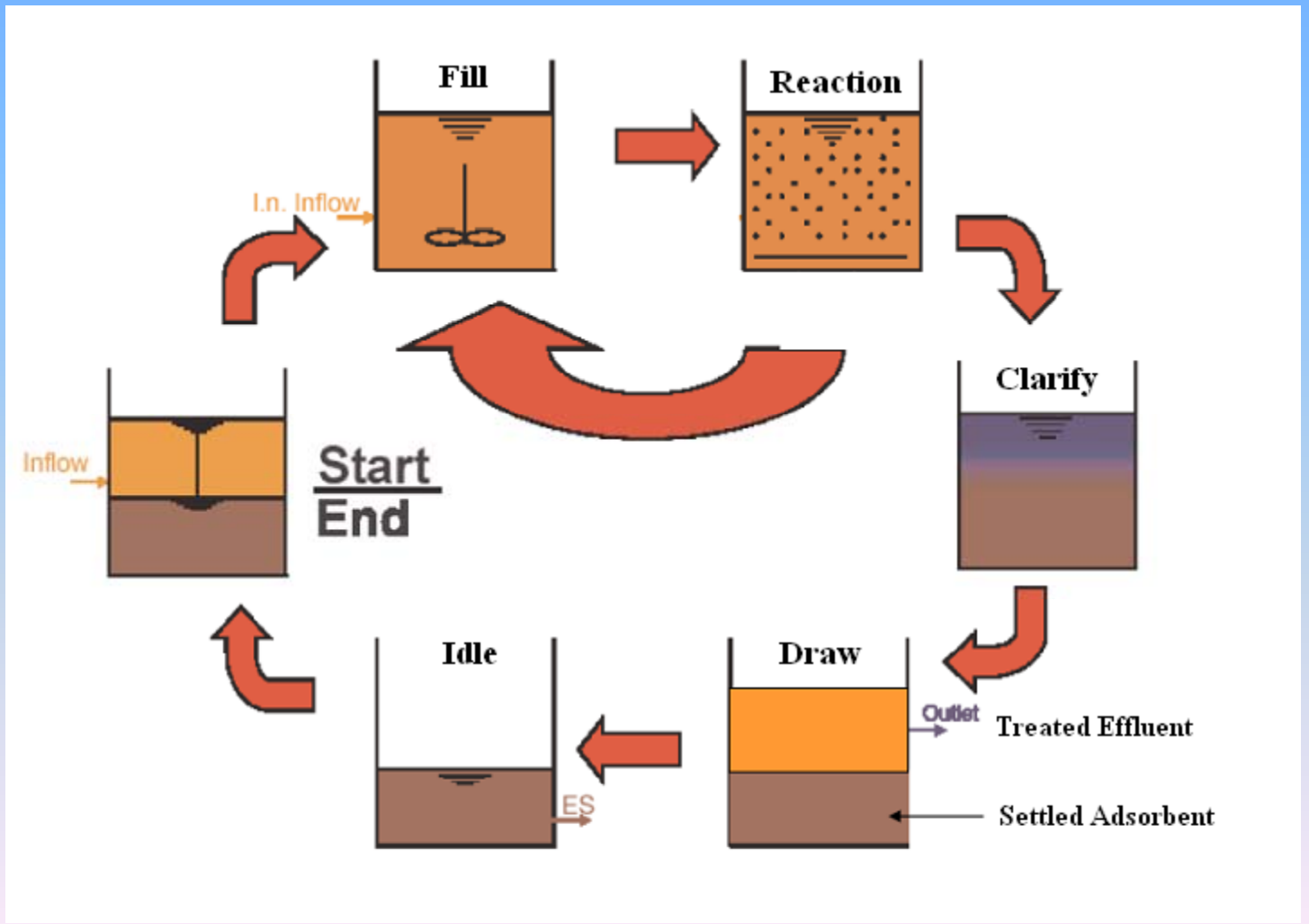
Phase II Results

Sequential Batch Reactor

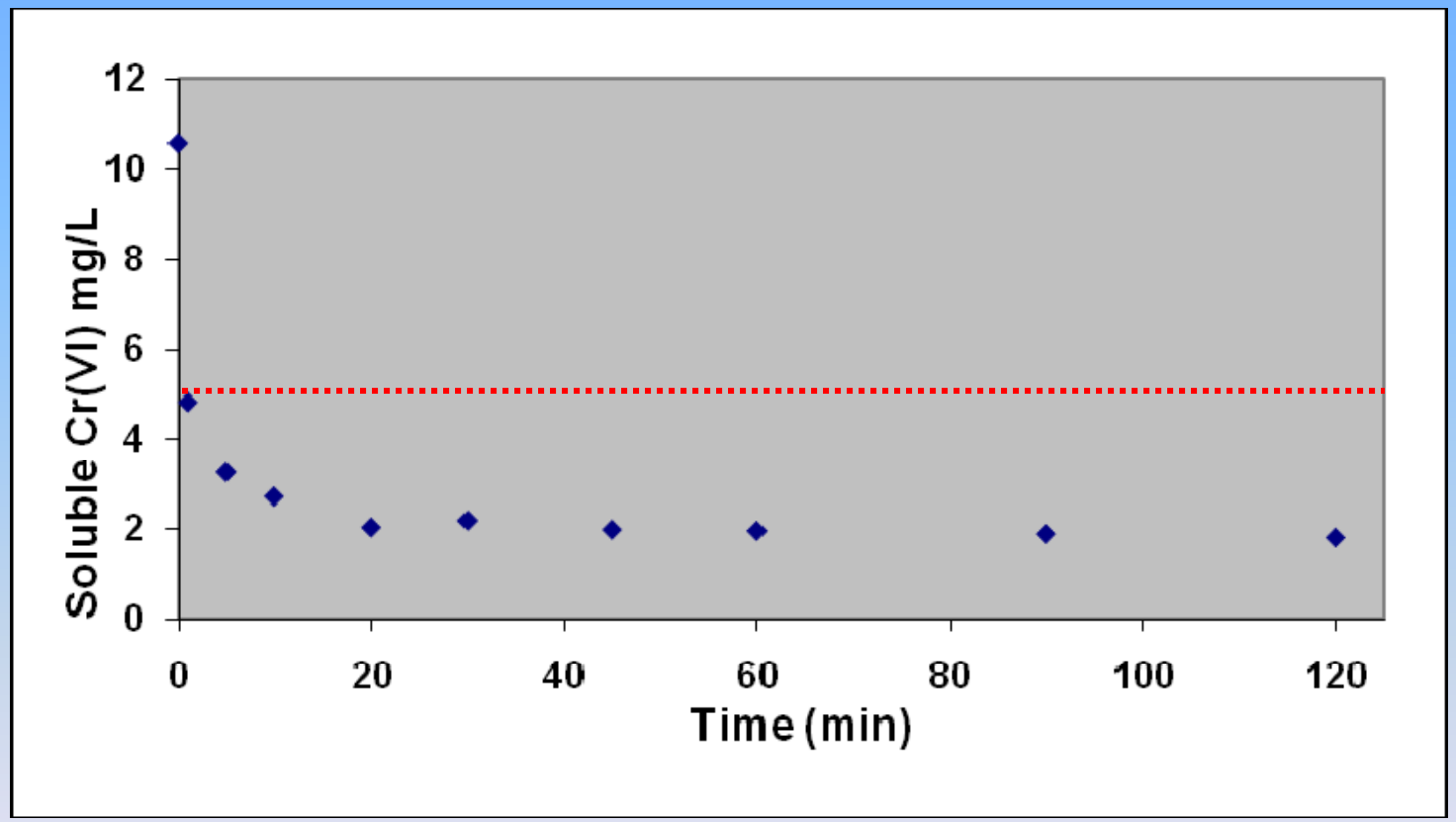
- SBR process utilizes a fill and draw reactor with complete mixing during the batch reaction. Clarification (settling of the adsorbent) occurs in separate tank.

- SBR operation consists of 5 steps
  - Fill
  - React
  - Clarify
  - Draw
  - Idle

SBR OPERATION

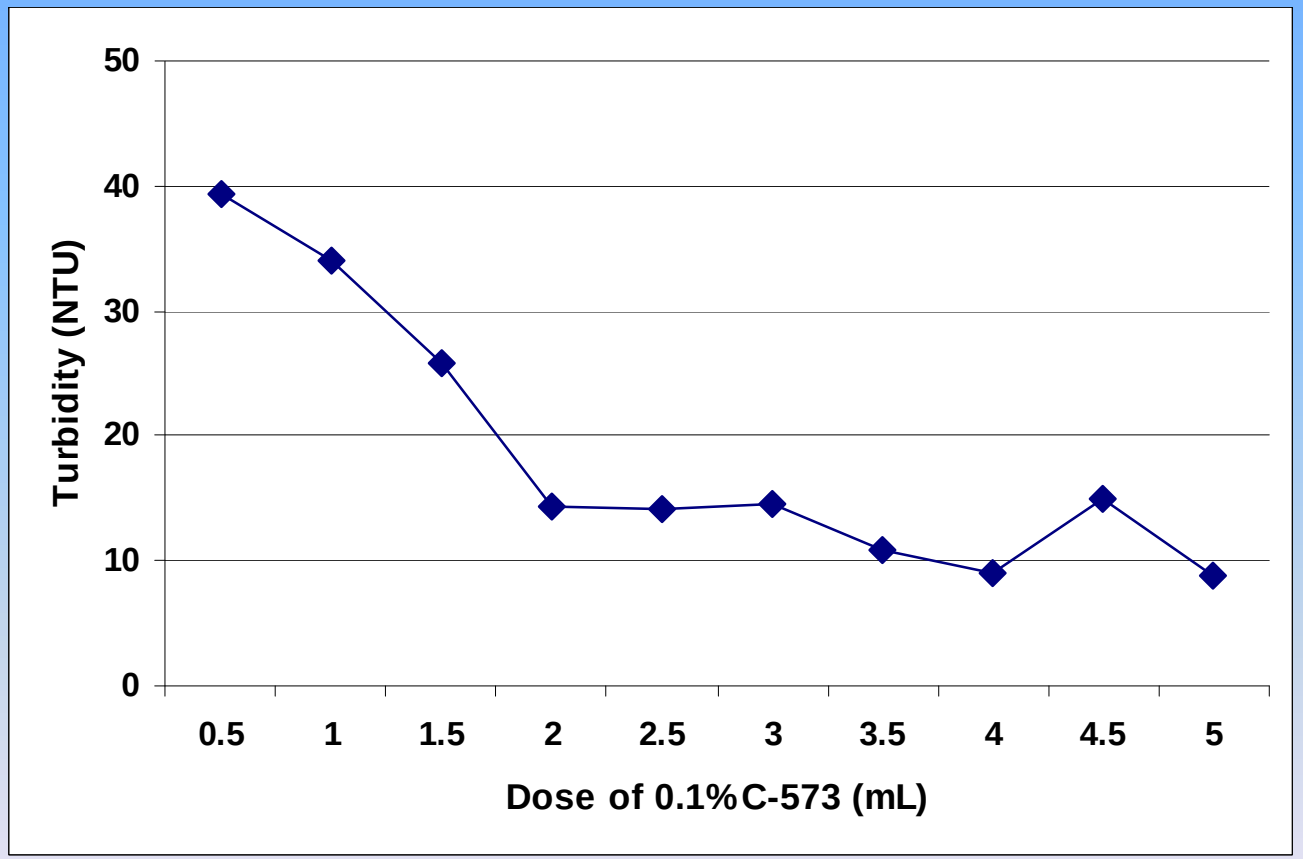


SIROM-A Kinetic Study



Chromium(VI) sorption kinetics using SIROM Sorbent A from standard Cr(VI) solutions. Solid to solution ratio was 1:10 (50 g WTR: 500 mL solution). Initial chromium load was 10 mg L^{-1}.

Clarification with C-573



Jar test data using cationic polyamine flocculant (C-573) with process water. Batch samples were prepared by mixing 500 mL of supernatant solution (1:2.5 SSR) with various doses of 0.1% C-573.

Process Water Treatment

Analyte	Conc. (mg L^{-1})	Discharge Limit (mg L^{-1})
pH	2.35	5 to 11
Ag	0.242	5
Al	11.0	50
As	0.023	1
Cd	2.26	0.5
Cr	12.8	5
Cu	1.89	5
Ni	2.21	5
Pb	2.82	2
Zn	0.172	5

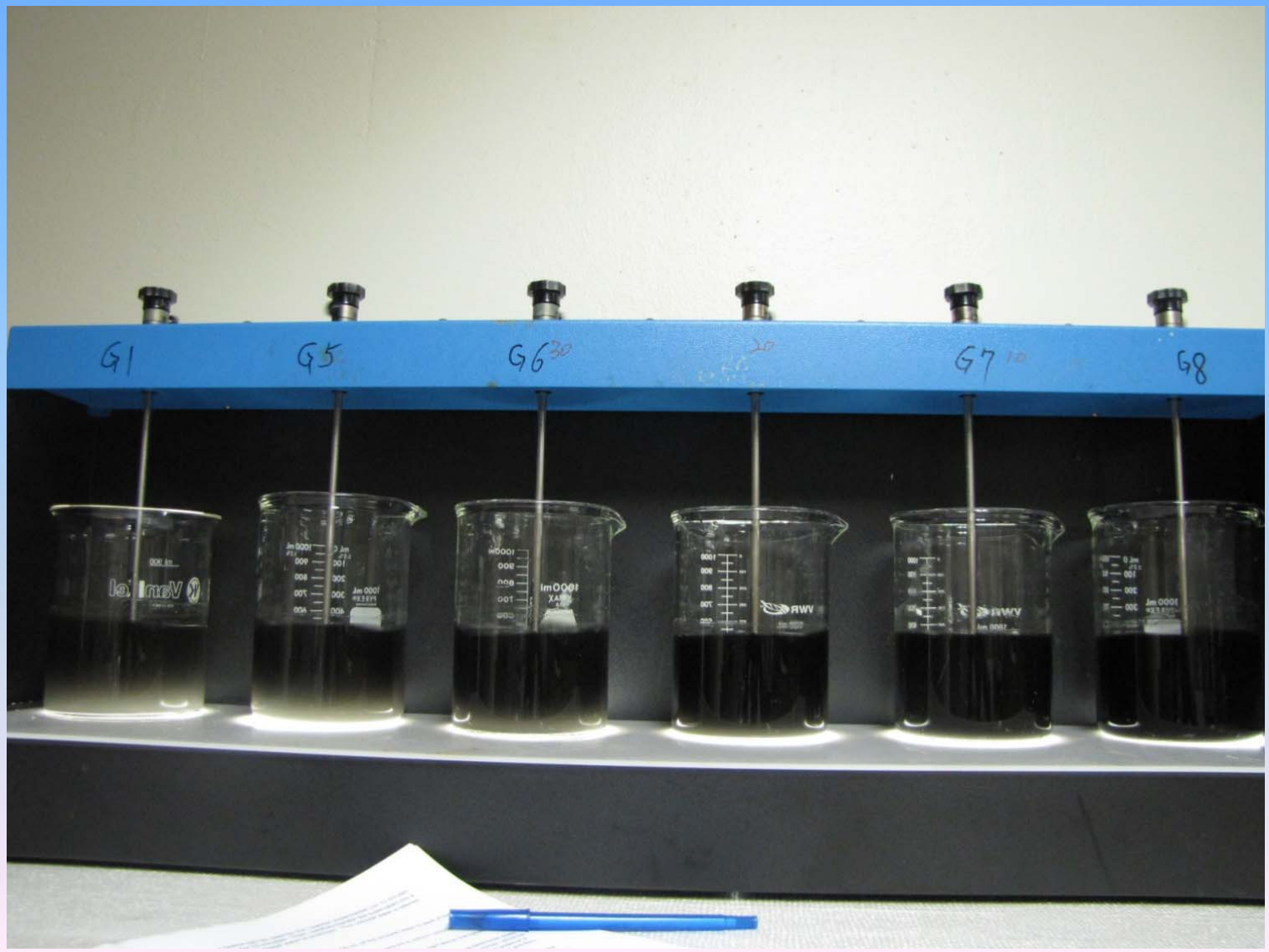
Re-Use of SIROM-A

Batch	Total metal concentration (mg/L)									
	Ag	Al	As	Cd	Cr	Cu	Fe	Ni	Pb	Zn
1	<0.05	<0.05	<0.05	<0.05	<0.05	0.12	0.08	<0.05	<0.05	<0.05
2	<0.05	<0.05	<0.05	<0.05	<0.05	0.12	0.08	<0.05	<0.05	<0.05
3	<0.05	<0.05	<0.05	<0.05	<0.05	0.12	0.08	0.07	<0.05	<0.05
4	<0.05	<0.05	<0.05	0.06	<0.05	0.11	<0.05	0.16	<0.05	<0.05
5	<0.05	<0.05	<0.05	<0.05	<0.05	0.12	0.06	0.25	<0.05	<0.05
6	<0.05	<0.05	<0.05	0.15	<0.05	0.20	0.10	0.26	<0.05	<0.05
7	<0.05	<0.05	<0.05	0.23	<0.05	0.21	0.11	0.38	<0.05	0.07
8	<0.05	<0.05	<0.05	0.37	0.14	0.20	0.16	0.60	<0.05	0.13
9	<0.05	0.12	<0.05	0.51	0.28	0.19	0.21	0.80	<0.05	0.14
10	<0.05	0.30	<0.05	0.74	0.58	0.24	0.39	1.13	<0.05	0.14

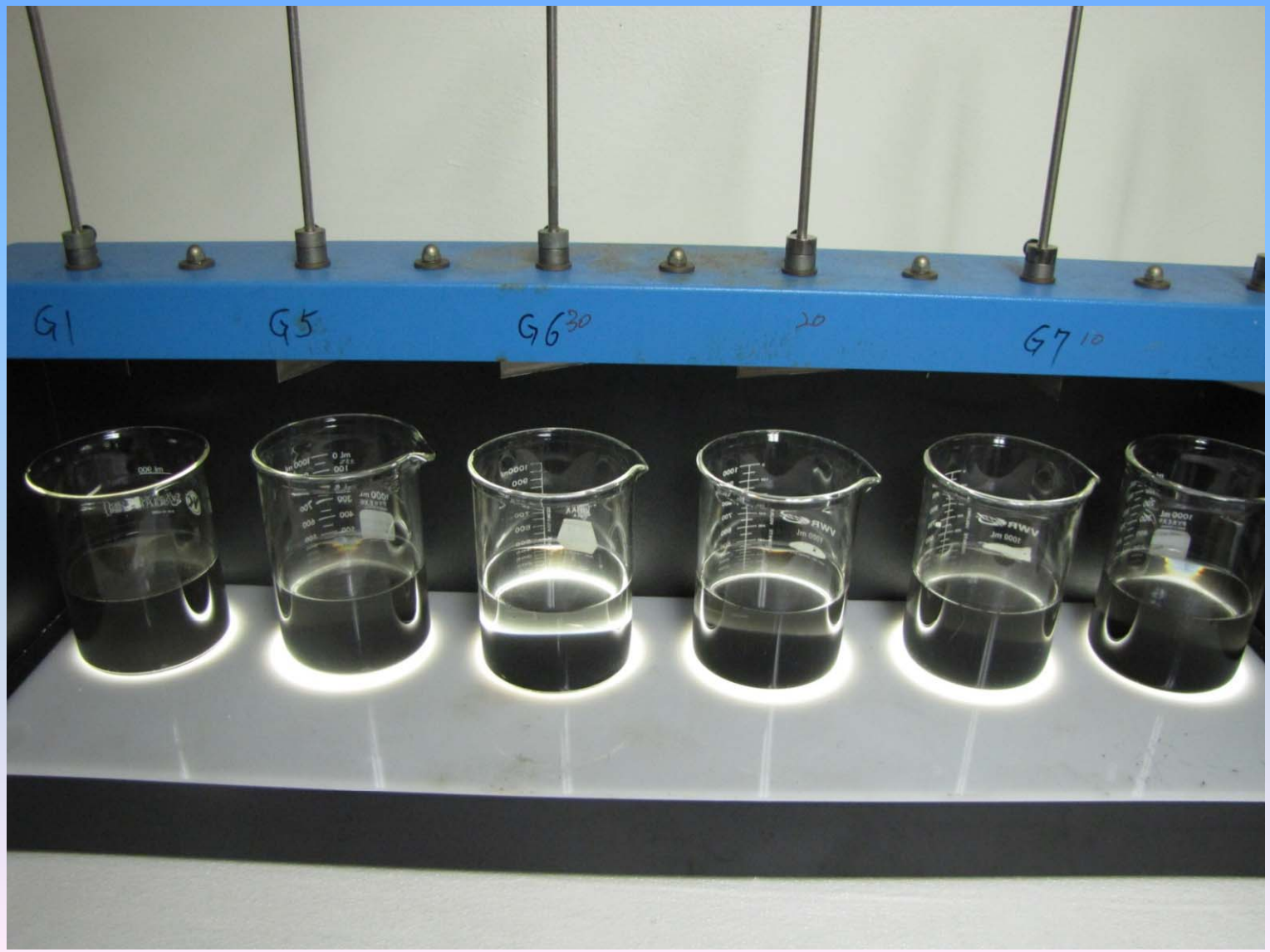
Re-Use of SIROM-A

Batch	NTU	pH
1	7.96	6.19
2	4.48	6.30
3	5.70	6.31
4	2.46	5.35
5	3.59	5.15
6	4.49	6.32
7	2.19	5.93
8	2.14	5.23
9	3.21	4.87
10	8.60	4.66

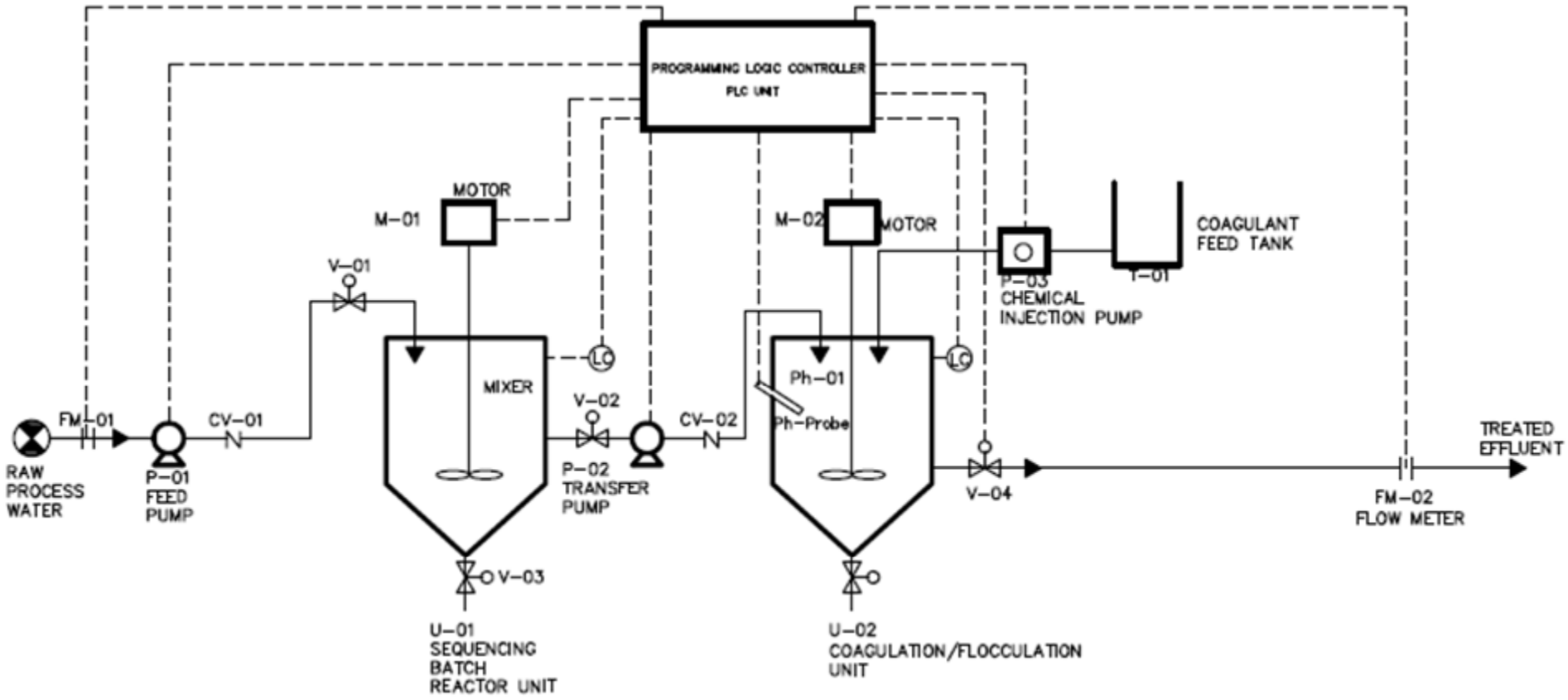
Bench Scale Apparatus



Bench Scale Apparatus



Skid Mounted Pilot Plant Unit



Pilot Development

- **Sequential Batch Reactor**
- **Portable / Deployable**
- **Small Footprint**
- **Same prototype for various applications**
  - Shipyard stormwater
  - Industrial process water
- **Should perform better under shipyard conditions**
  - Sample Matrix
  - Contaminant levels

Transition Partners

- **Navy Transition Assistance Program**
  - Market research
  - Identification of potential partners
    - NSRP meetings
    - Navy Opportunity Forum
- **Shipyards prototype demo**
  - Naval and Private (2 shipyards)
  - Stormwater metals
- **StandardAero prototype demo**
  - Similar metals issue as in shipyards

Prototype Demonstration Plan at Partner Facilities

Objectives

- Demonstrate treatment efficiency and ease of operation (both shipyard and industrial sites)
- Optimize operation (fill, react, settle, etc.)
- Identify potential operational problems & provide appropriate solutions
- Develop kinetics and scale-up design equations
- Determine treatment costs ($/1,000 gal water treated)

Commercialization Considerations

- **Need**
  - US Navy shipyards and other DoD facilities,
  - Private shipyards,
  - Aircraft and engine servicing plants,
  - Metal finishing industries,
  - Recycling of water in boat washing facilities
  - Firing ranges for the removal of lead,
  - Commercial developments for the treatment of stormwater contaminated with heavy metals and phosphorus

- **Market Drivers**
  - The main market driver is environmental regulations,
  - Also, need for lower treatment costs.

Commercialization Considerations

- **Value Proposition**

  Lower the treatment costs by a minimum of 30-50% while meeting or exceeding the environmental/process requirements.

- **Performance Criteria**
  - Compliance with environmental regulations
  - Low cost
  - Low frequency of sorbent replacement
  - Ease of operation

- **Rate of Market Growth**

  Accounting for new environmental regulations related to stormwater and water recycling from boat washing facilities it is estimated that the rate of market growth over the next five years will be around 15-20%.

WHERE WE ARE

- **OPTIMIZED SORBENT FOR MAXIMUM METAL RETENTION CAPACITY**
- **FINISHED PROTOTYPE DESIGN**
- **IDENTIFIED INDUSTRY PARTNERS FOR PILOT STUDIES**
  - **Standard Aero: Definite**
  - **Norfolk Shipyard: Likely**

REMAINING TASKS IN PHASE-II

- ***Finish prototype assembly***
- ***Deploy prototype on-site for pilot study***
- ***Identify Industry Sponsors for SBIR Phase-III - Full Scale Demonstration Study***
- ***Submit NSRP – ASE Proposal for additional funding***
- ***Submit SBIR Phase-III Proposal (estimated $800K - $1M)***
  - ***Funding Component 1: NSRP-ASE***
  - ***Funding Component 2: Industry Partner***
  - ***Funding Component 3: Navy (up to 25% of the total project cost)***

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