

RECOVERY OF METALS FROM WASTEWATER AND OIL

**Dr. Rakesh Govind
PRD Tech, Inc. and
University of Cincinnati
Cincinnati, OH 45212**

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Metal Finishing Wastewater Treatment

- **Variety of metals are found in metal finishing wastewaters (chromium, zinc, cadmium, copper, iron, etc.) ;**
- **Metals are also present in Acid Mine Drainage (AMD)**
Example: The Berkeley Pit, Butte Montana
Largest superfund site in the US;
Contains more than 25 billion gallons of AMD with a daily incremental increase of approximately 3 million gallons resulting in a rise of 12 feet every year.

BERKELEY PIT, BUTTE, MT



Element	[Conc] _{avg(ppm)}	Price (\$/metric-ton)	Year 07 (\$)	Year 10 (\$)	Year 15 (\$)
Al	396.28	2650	\$119,116,939	\$136,508,012	\$158,246,854
Mn	337.16	450	\$17,209,600	\$19,722,201	\$22,862,953
Fe	711.06	210	\$16,937,557	\$19,410,440	\$22,501,544
Cu	220.93	7990	\$200,233,139	\$229,467,178	\$266,009,726
Zn	905.24	3515	\$360,926,799	\$413,622,111	\$479,491,252
			\$714M	\$819M	\$950M
α -FeOOH	711.06	4408	\$355,527,380	\$407,434,377	\$472,318,124
			\$1.05B	\$1.20B	\$1.40B

BIORECOVERY OF METALS

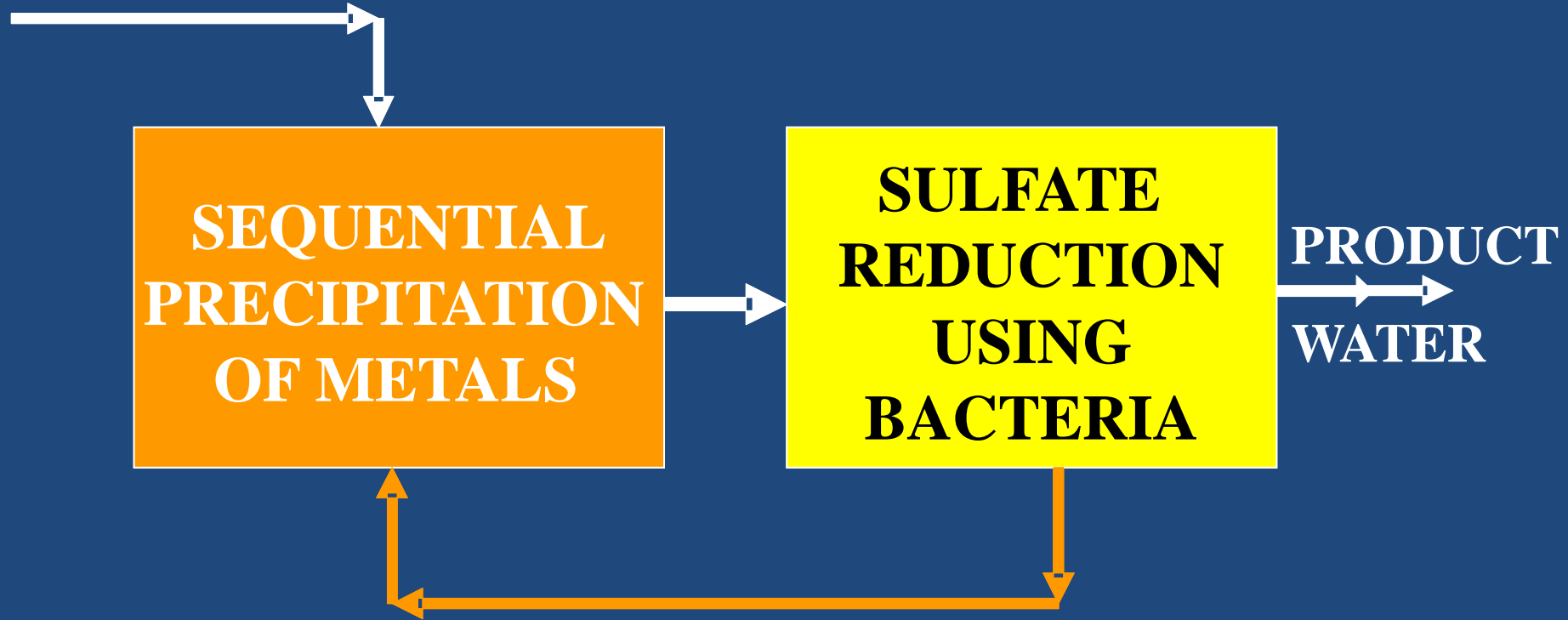
ACID MINE DRAINAGE

SEQUENTIAL
PRECIPITATION
OF METALS

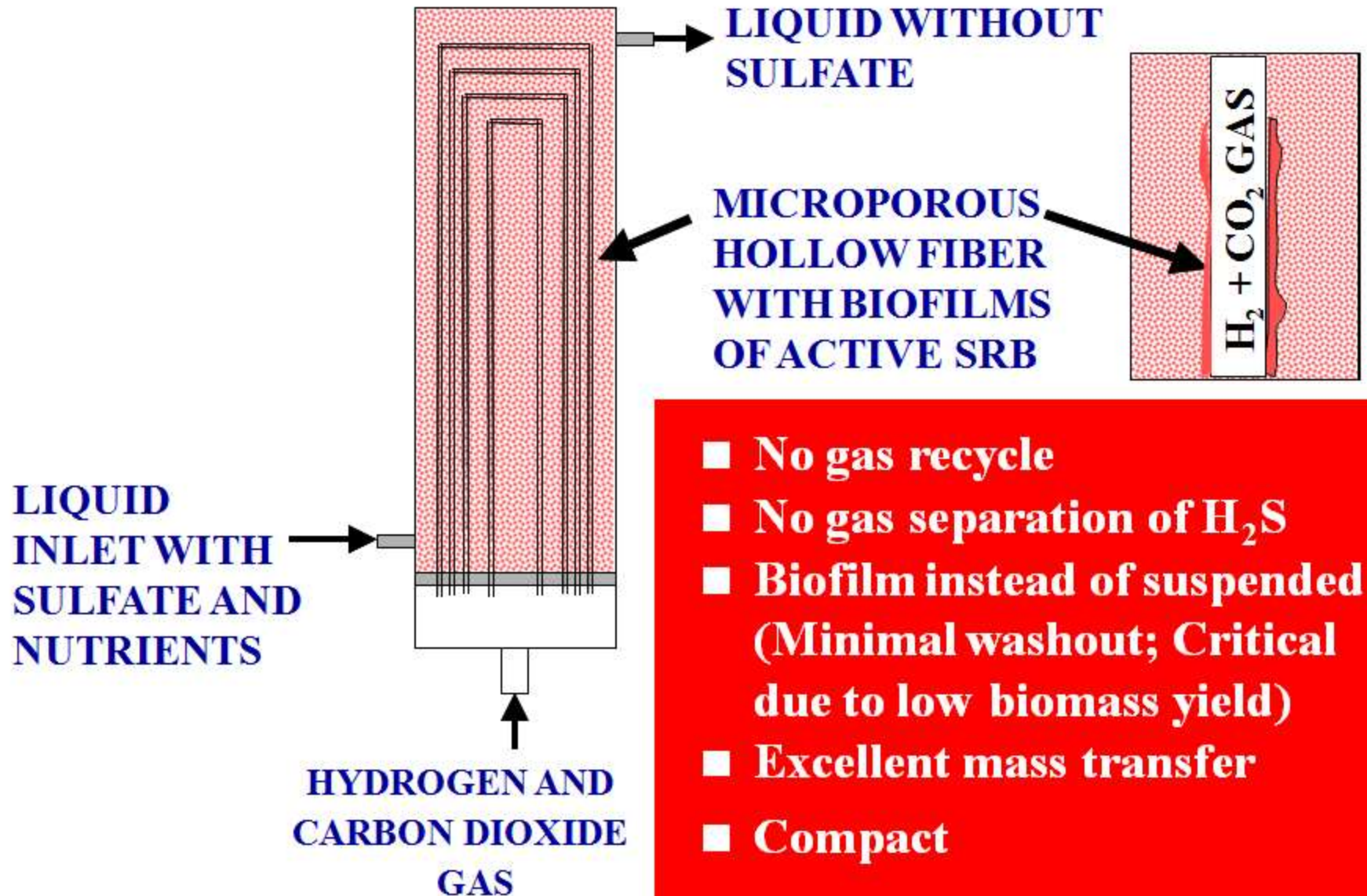
SULFATE
REDUCTION
USING
BACTERIA

PRODUCT
WATER

BIOGENIC HYDROGEN SULFIDE

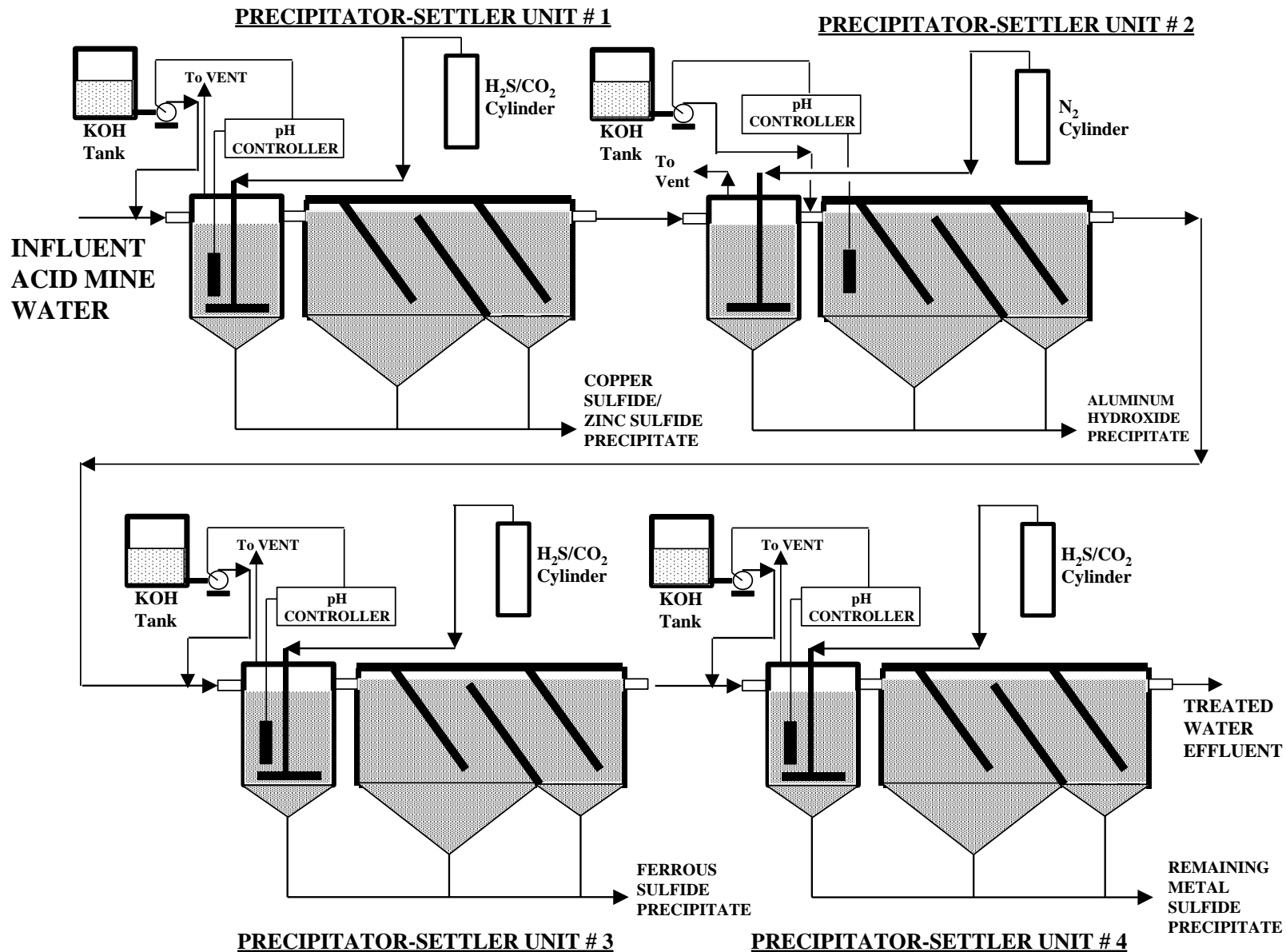


MEMBRANE BIOREACTOR



- **No gas recycle**
- **No gas separation of H₂S**
- **Biofilm instead of suspended (Minimal washout; Critical due to low biomass yield)**
- **Excellent mass transfer**
- **Compact**

TREATMENT PROCESS



TREATMENT PROCESS PERFORMANCE

Experiment Number	Precipitator-Settler Unit # 1			Precipitator-Settler # 2		Precipitator-Settler # 3		Precipitator-Settler # 4	
	pH	Cu	Zn	pH	Al	pH	Fe	pH	Mn
1	2.21	100.0%	99.9%	4.85	97.0%	6.28	100.0%		
2	2.24	100.0%	100.0%	4.88	96.8%	6.28	100.0%		
3	2.21	100.0%	99.9%			6.15	97.6%		
4	2.38	100.0%	100.0%	4.60	82.1%	5.74	100.0%		
5	2.25	100.0%	100.0%	4.78	86.7%	6.42	100.0%	9.83	100.0%
6	2.22	100.0%	100.0%	4.84	88.8%	12.84*	100.0%	9.52	100.0%
7	2.21	100.0%	100.0%	4.83	95.2%	12.91*	100.0%		
8	2.17	100.0%	100.0%	5.09	89.9%	6.05	100.0%	9.52	100.0%
9				4.26	84.6%				
10	2.27	100.0%	99.9%						
11	2.18	99.9%	99.9%						
12	2.56	100.0%	99.9%	5.23	92.0%	6.19	100.0%	10.34	100.0%
13	2.76	100.0%	99.9%	5.31	96.1%	6.33	99.6%	10.27	99.0%
14	2.71	100.0%	99.5%	5.39	96.1%	6.18	99.8%	9.93	95.1%
15	2.15	100.0%	99.8%	5.46	97.1%	6.29	99.9%	9.94	99.1%
16	2.45	100.0%	99.8%	5.13	92.9%	6.58	99.6%	9.39	96.3%
17	2.35	99.9%	99.9%	5.48	97.1%	6.36	99.8%	9.42	100.0%
18	2.37	99.9%	99.9%	5.94	99.2%	6.33	100.0%	10.16	99.0%
19	2.41	100.0%	99.8%	4.65	77.1%	6.46	100.0%	9.17	99.3%
20	2.50	99.8%	99.7%	5.13	92.8%	6.09	99.7%	10.48	100.0%
21	2.29	99.9%	99.9%	5.68	98.5%	6.22	99.6%	9.74	89.2%

* Denotes abnormal point

PURITY OF PRECIPITATES PRODUCED

Experiment Number	Copper / Zinc Sulfide			Aluminum Hydroxide		Ferrous Sulfide		Manganese Sulfide
	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.	Meas.	Calc.
1		98.2%		97.0%	93.9%	92.0%		
2		99.5%		96.8%		79.7%		
3		99.7%			94.2%	92.4%		
4	96.8%	95.8%	66.1% *	82.1%		93.9%		
5	99.2%	97.1%	68.2% *	86.7%	54.4%	66.7%	33.1%	28.8%
6	98.3%	98.0%		88.8%	78.3% *	34.3% *	51.0%	65.6%
7		98.6%		95.2%		35.2% *		
8		98.2%	96.8%	89.9%	94.9%	92.4%	35.3%	50.9%
9	97.4%			84.6%				
10	99.2%	99.8%						
11		79.6%						
12	98.6%	98.1%	94.3%	92.0%		55.5%		7.2%
13		81.7%		96.1%		67.5%		10.1%
14	98.7%	99.7%	93.2%	96.1%	66.8%	59.6%	14.0%	9.2%
15		99.7%		97.1%		57.4%		8.1%
16	98.9%	99.5%	95.2%	92.9%	58.4%	61.9%	8.0%	12.0%
17		77.2%		97.1%		57.4%		34.3%
18	98.7%	99.7%	89.1%	99.2%	63.3%	58.1%	9.2%	8.9%
19		99.8%		77.1%		61.6%		33.7%
20		99.2%		92.8%		70.5%		7.5%
21	99.0%	86.9%	85.1%	98.5%	59.3%	63.6%	13.7%	5.6%

METAL REMOVAL EFFICIENCY FROM BERKELEY PIT WATER

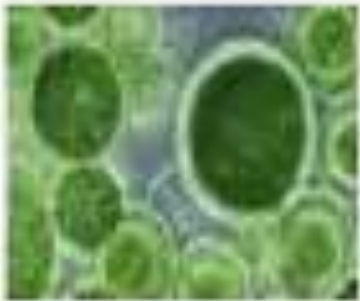
Expt. No.	Al	Ca	Cd	Co	Cr ⁺	Cu	Fe	Mg	Mn	Ni	Zn
5	100%	46%	100%	100%	80%	100%	100%	50%	100%	100%	100%
6	100%	16%	100%	100%	58%	100%	100%	19%	100%	100%	100%
8	100%	20%	100%	100%	71%	100%	100%	32%	100%	100%	100%
12	99%	53%	100%	100%	80%	100%	100%	36%	100%	100%	100%
13	99%	57%	99%	97%	55%	100%	100%	32%	100%	97%	100%
14	99%	47%	100%	100%	95%	100%	100%	20%	99%	91%	100%
15	99%	53%	100%	100%	75%	100%	100%	20%	100%	100%	100%
16	99%	41%	100%	100%	72%	100%	100%	20%	99%	90%	100%
17	99%	29%	100%	100%	35%	100%	100%	12%	100%	100%	100%
18	99%	53%	100%	100%	98%	100%	100%	19%	100%	100%	100%
19	99%	19%	100%	100%	36%	100%	100%	9%	100%	88%	100%
20	99%	50%	100%	100%	66%	100%	100%	49%	100%	91%	100%
21	99%	35%	100%	100%	41%	100%	100%	18%	98%	89%	100%

* Based on instrument detection limit

HYDROTHERMAL LIQUEFACTION (HTL)

Waste Biomass

Algae



Wood



Coal



Sewage



Manure



Bio-Oil



Alaska



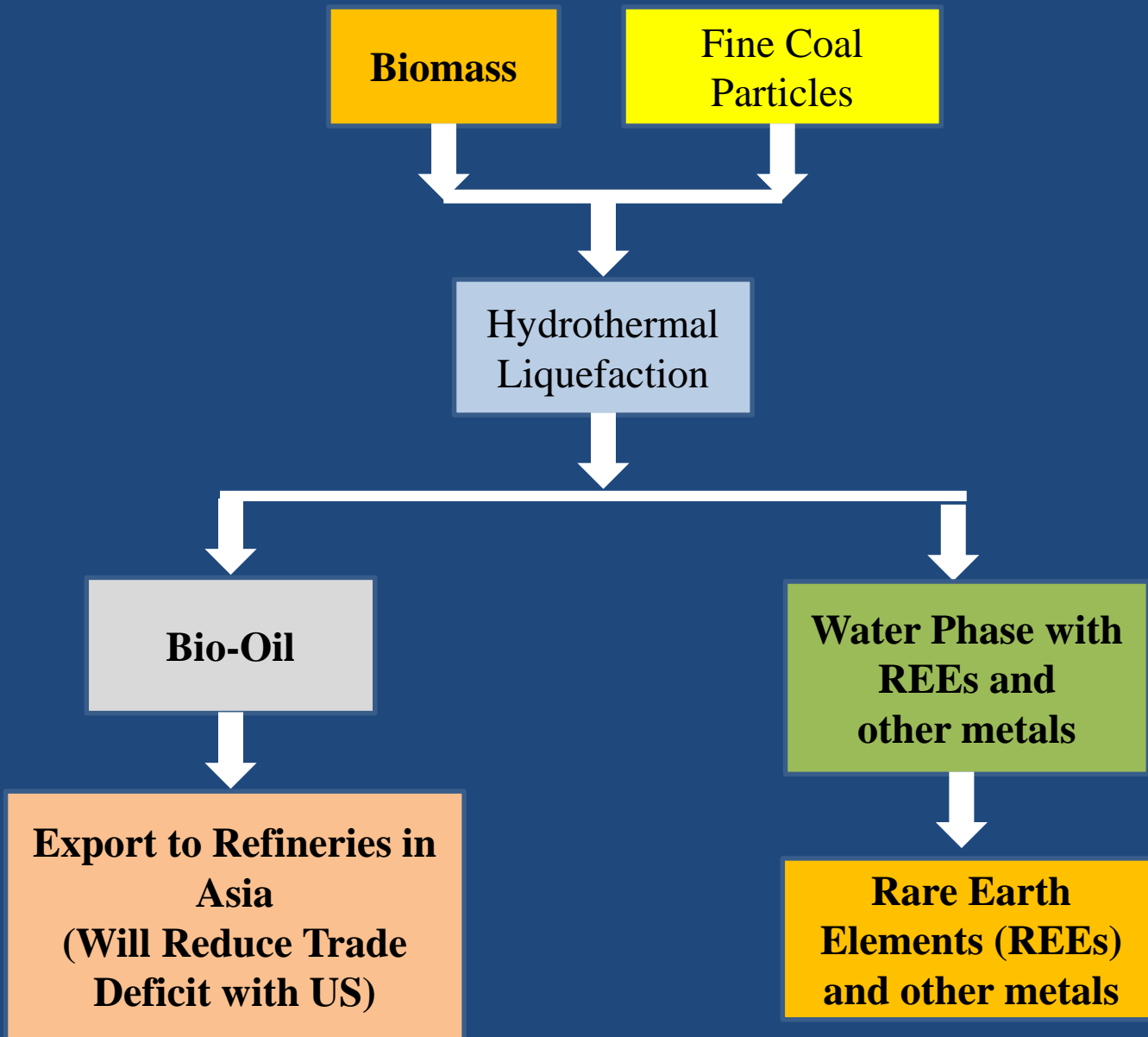
Hawaii



<https://www.netl.doe.gov/research/coal/rare-earth-elements>

U.S. Department of Energy analyzed hundreds of coal and coal by-product samples and found highest rare-earth assays in the northern Appalachian region

OVERALL PROCESS SCHEME FOR COAL



CONCLUSIONS

- Metals can be recovered from Acid Mine Drainage using the sulfide precipitation process, wherein the sulfide is generated using Sulfate reducing Bacteria (SRBs)
- Experimental results obtained using Berkeley Pit Acid Mine Drainage has shown that Cu, Zn, Fe, Mn and Al can be selectively separated at high purities using the sulfide precipitation process
- It is proposed to convert coal into Bio-Oil using Hydrothermal Liquefaction in conjunction with waste biomass to get partially carbon-neutral oil (exported to Asia) and Rare Earth Elements and other metals in the water phase
- Rare Earth Elements can be easily extracted from the water phase after Hydrothermal Liquefaction of Coal