COPPER CMP TREATMENT OPTIONS and CHALLENGES

Lyle Kirman
Kinetico Incorporated

9/25/01

Goals and Objectives

- Implementation of Copper Plating and CMP Tools without environmental complications
- Cost-Effective, Reliable, Systems
- Options for Water Recycling
- Flexibility for Future Chemistry Changes
- Lowest Cost of Ownership

Strategy

- Answer the critical questions (the answers may be customer-specific)
- Understand the Critical Parameters
- Choose the most effective design to meet/exceed customer goals
- Anticipate future needs and goals.

CRITICAL QUESTIONS THAT DETERMINE THE DESIGN

- Is the goal to precipitate copper with CMP solids or to remove copper separately?
- Will Polish and Rinse flows be treated together or separately?
- Central treatment or treatment at each tool?
- Segregated Copper CMP, or mixed with Oxide and Tungsten?

CRITICAL QUESTIONS, CONTINUED

- For Central Systems Only, integrate with Plating Tools, or no integration?
- Water Recycling or no Water Recycling?
- If Water is Recycled,
  - To Low Quality? (scrubbers, cooling towers)
  - To High Quality? (Return to CMP polish loop)
- How much Space is Available?

Will Copper be intentionally precipitated with other CMP Solids?

- If the answer is “NO”, then
  - pH adjustment and IX, or other copper removal is req’d.
  - Oxidizer removal is recommended prior to IX.
- If the answer is “YES”, then
  - Chemicals in addition to pH adjustment will be req’d.
  - Oxidizer removal may also be req’d.

Will Polish and Rinse flows be treated together, or separately?

- Combined treatment may be favored for a compliance only system with no recycling.
- Separate rinse treatment is favored if water recycling is desired, especially if it needs to be high quality.
  - High TSS, TDS, and TOC make recycle of the Polish waste flow more difficult and expensive.
  - TDS concentrations in combined flow are expected to be too high to use DI to recycle economically.

Will Polish and Rinse flows be treated together, or separately?

- Combined Treatment is probably cheaper (one system instead of two systems)
- Several designs can treat and recycle the combined flows.

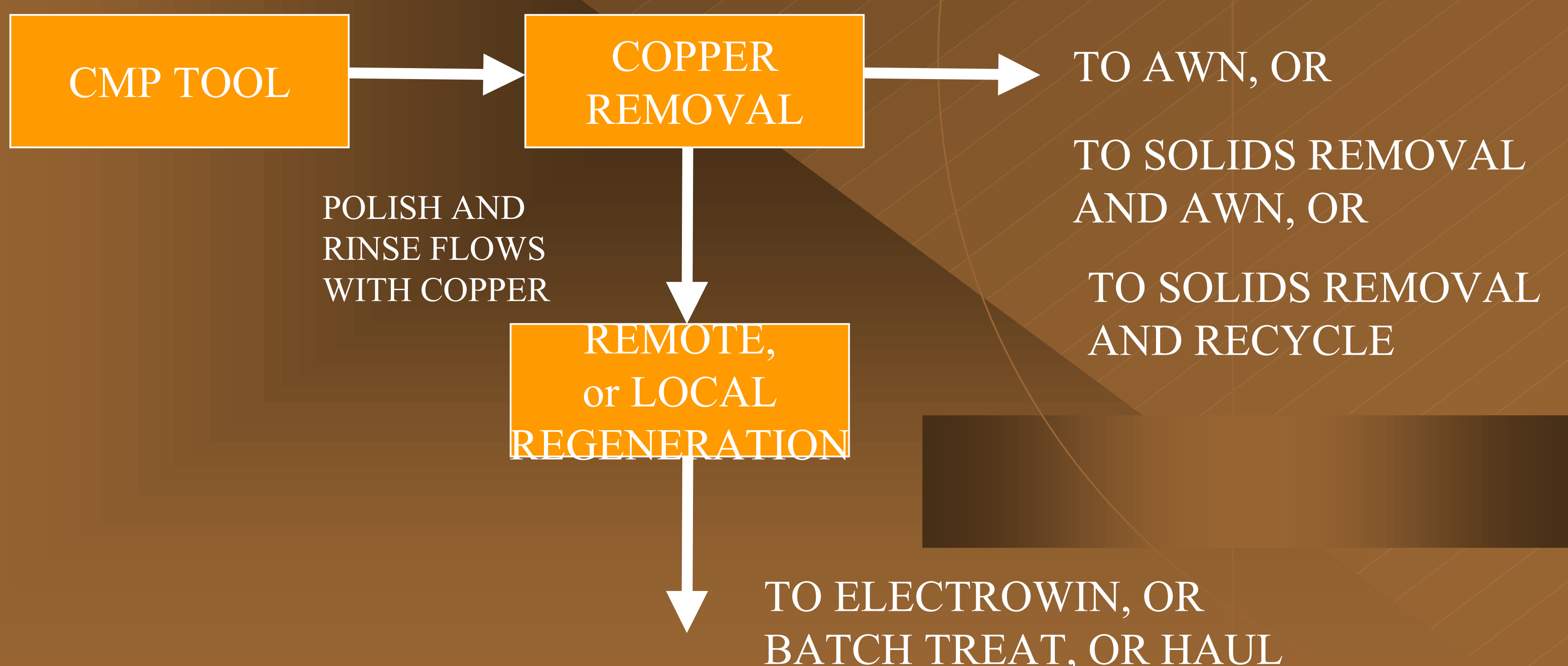
Will Polish and Rinse flows be treated together, or separately?

- Recycling of the combined rinses is possible with the MF / IX / RO design, if
  - A central system is designed, and
  - An or RO is used for TDS and TOC removal, and
  - Either medium Quality is needed, or additional polishing is added for high quality.

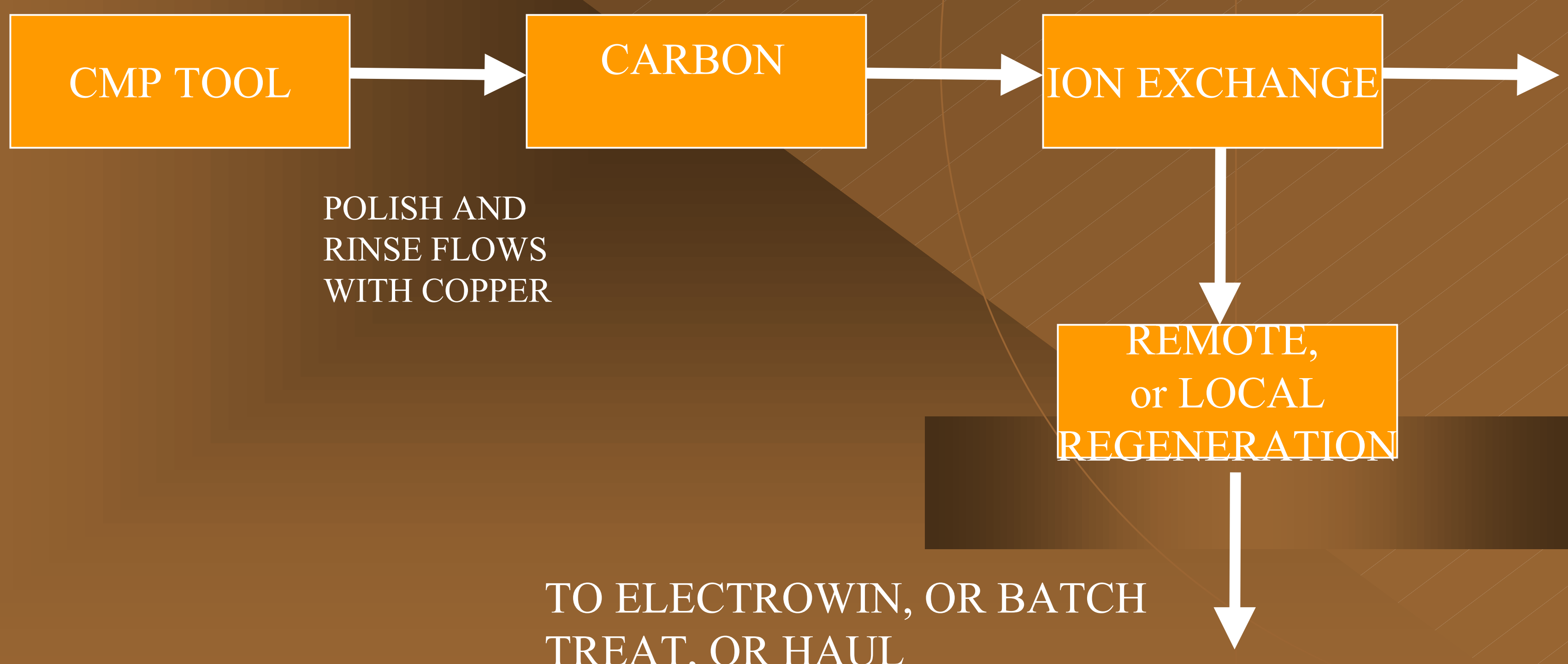
Central System or a System at each Tool?

- Central systems have economy of scale.
- Solids removal at each tool would be very expensive and require a lot of valuable Fab or Subfab space.
- A hybrid approach may be more practical and economical.
  - Copper removal at the tool.
  - Central system for Recycling. (could add at a later time)

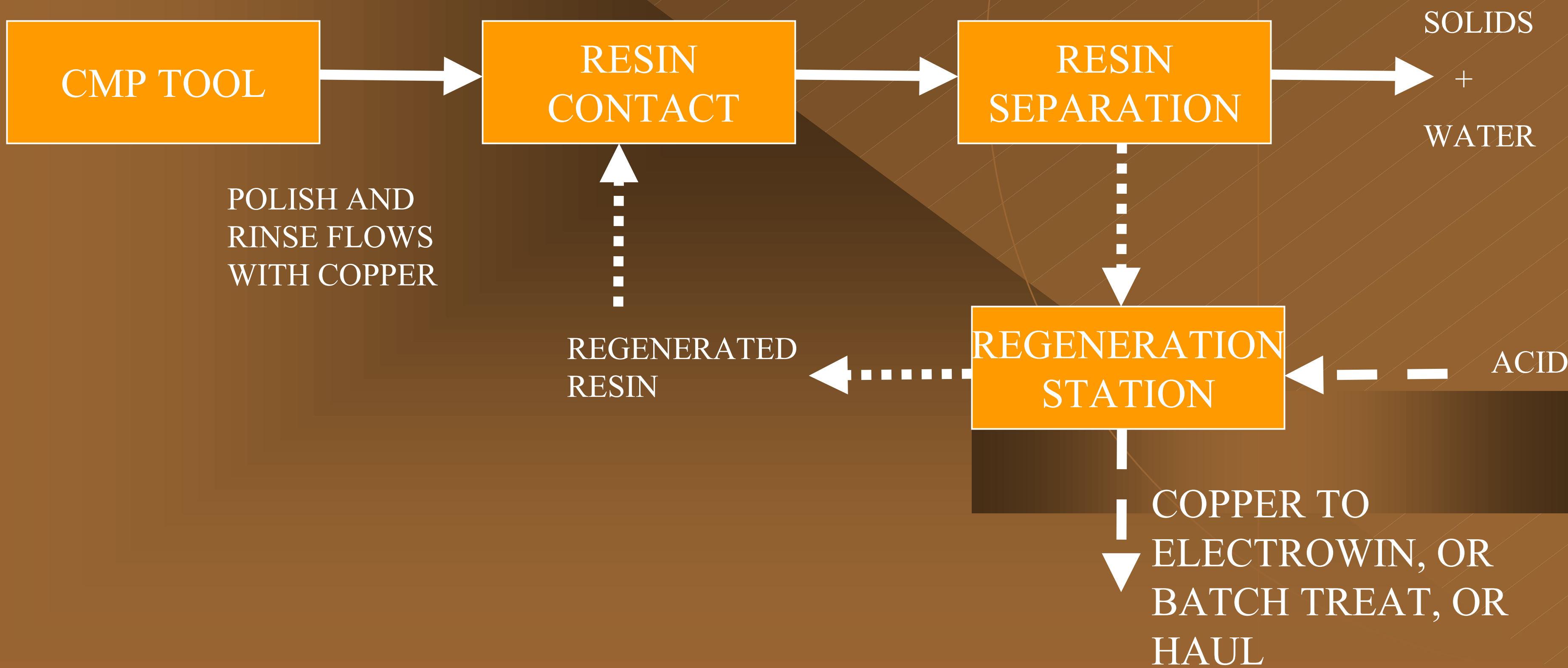
Hybrid System = Copper Removal at Tool plus Central Solids Removal and/or Recycle



Hybrid System = Copper Removal at Tool Concepts



Hybrid System = Copper Removal at Tool Concepts Under Development



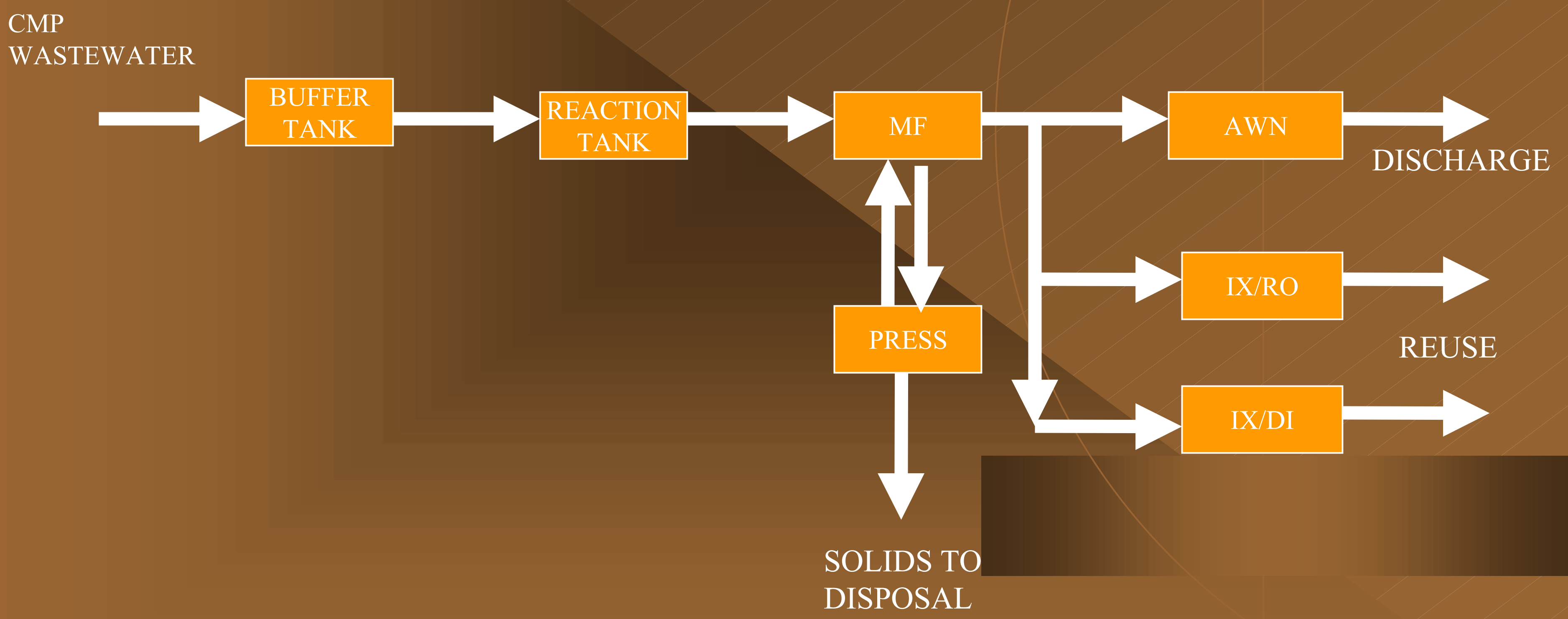
Segregated Copper CMP or mixed with Oxide and/or Tungsten CMP?

- Segregated Copper is easiest and offers more design choices.
- Hi Silica Concentrations in Oxide CMP wastewater complicates any recycling design except one.
  - Silica can be precipitated in the solids-removal but this adds TDS and generates huge sludge volumes.
  - TDS after solids removal may be too high for DI.
  - Residual Silica limits conventional RO Recovery.
- The MF/ IX/ RO design can treat and recycle mixed CMP flows.

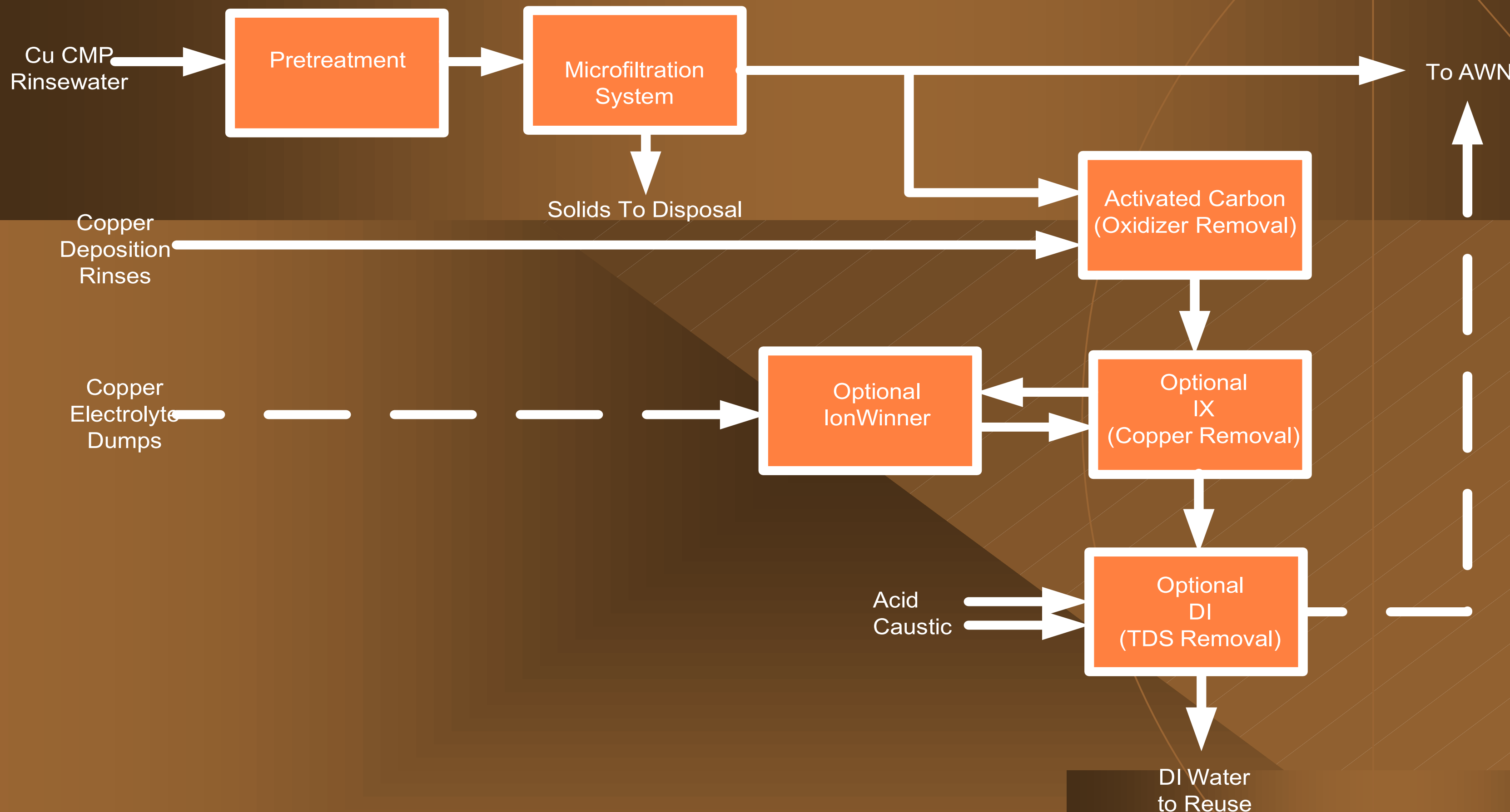
For Central Systems Only: Integration with Copper Plating Tool Wastewater? or no Integration?

- Integrated approach avoids duplication of systems.
  - The same IX system for copper can be used for filtered CMP, and Plating Tool rinses.
  - The same Electrowinner can be used for Copper Electrolyte dumps and IX Regenerations.

Recommended Designs for Central Systems



General Process Flow with or without Integration of Copper Plating Tool Wastes for Low TDS Rinse Flows



This drawing is for sales purposes only. It is not an engineering drawing. Actual details may vary.

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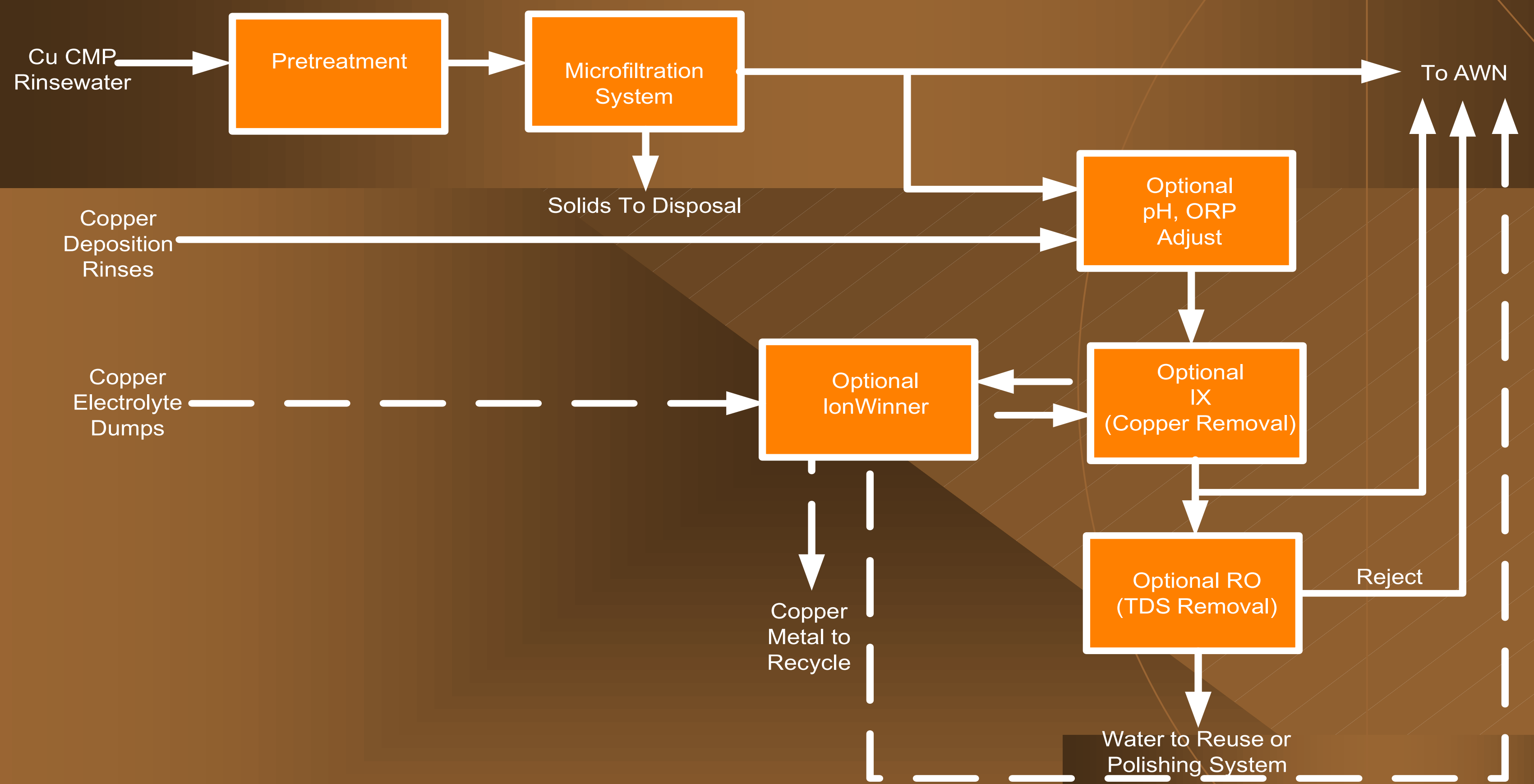
Drawing #P05204A2

General Process Flow with or without Integration of Copper Plating Tool Wastes for High TDS Rinse Flows



This drawing is for sales purposes only. It is not an engineering drawing. Actual details may vary.

Drawing #P05204A1

Will Water Recycling be part of the Design?

- Recycle to Medium Quality? (Scrubbers or Cooling Towers)
- Recycle to High Quality? (Return to CMP polishing loop)

CRITICAL PARAMETERS THAT AFFECT THE DESIGN

- Feed Analysis
- Discharge Limits
- Water Cost
- Water Quality
  - Local Tap Water
  - Quality of Recycled Water Desired

Copper CMP Wastewater Analyses

	8-9 DATA	8-10 DATA	BID DOC.	OTHER DATA
TSS	1000	2-2800	1300-6000	3150
TDS	200	450-600	500-600	700-800
TOC	200	300-400	35-100	300-400
TOTAL Cu	20	7-15	20	17
FILT. Cu	4	3.5-6	15-100	7

Copper CMP Wastewater Analyses/ Specifications from 3 Customers

TSS	390	<10,000	570-1133
TDS	540	<1325	171
TOC	55	220-600	UNK
TOTAL Cu	3.1	10-120	<20
FILT. Cu	2.9	10-120	<20

TYPICAL OPERATING COSTS FOR COPPER IX, Per Lb of Copper or Per 1000 Gallons

COST FACTOR	50 mg/L	25 mg/L
Labor	$.42	$.83
Electricity	.22	.45
Chemicals	.90*	.90*
Resin Replacement	.08	.16
Other Repairs/Replacements	.20	.40
Total per Lb copper	$1.82	$2.74
Total per 1000 gallons	$ .51	$ .46

* Can be Reduced by 30% by Acid Reuse at Remote or Central Systems

FOR Low TDS DI RECYCLING, WHY CATION → CATION → ANION?

- Consider a typical analysis.
  - 6 mg/L soluble copper, and approx. 500 mg/L TDS.
  - 6 mg/L of Cu = 15.2 mg/L as $CaCO_3$.
  - The total cation load = 500/15.2 = 32.9 times the copper load!!
- The CCA design uses the first cation to remove and concentrate Copper, the second cation and anion to remove the rest.
- This means Less and More Concentrated Copper Waste Volume, also more Efficient Electrowinning.
- Other designs may produce 30 times more (and more dilute) Copper Waste!!!

TABLE 9 - WATER QUALITY ACHIEVED BY SEPARATE BED DEIONIZATION

PARAMETER	AS REC'D	AFTER REDUCTION	AFTER FILTRATION	AFTER CARBON	AFTER DI
TDS	540*	na	420	na	<10
CONDUCTIVITY	151	892	840	na	5.4
TOC	55	na	29.4	17	0.4
Cu, TOTAL	3.06	na	3.18	na	0.02
TKN	17	na	16	na	<1
TURBIDITY	28	na	0.1	na	<0.1
pH	7.5	2.9	2.85	na	6.3
SiO2	56	na	4.3	na	0.1

* TSS that go through a 1 u filter are counted as TDS

WHY HERO REVERSE OSMOSIS FOR HIGH TDS WATER RECYCLING?

- Highest Water Recovery % (typically > 90%).
- Much Higher TOC Rejection than Conventional RO.
- Very Low Chemical Use.
- Can operate in High Soluble SiO_2 wastewaters.
- Can handle mixed Copper and Oxide and Metal CMP Wastewaters.

TABLE 10- WATER QUALITY FOR HIGH SiO2 CMP WATER AFTER RO

PARAMETER	AS REC'D	AFTER FILTRATION	AFTER DEGAS + Na OH	AFTER 1stRO ARRAY	AFTER 2ndRO ARRAY	RO CONCENTRATE
TSS	240	NA	NA	NA	NA	NA
TOTAL SOLIDS	400	170	150	20	50	1550
CONDUCTIVITY	NA	221	246	71	126	1800
TOC	NA	0.7	0.4	0.3	0.3	0.1
CALCIUM	NA	3.18	0.14	<.01	<.01	0.04
pH	9.22	8.7	10.5	10.6	10.7	10.6
SiO2	NA	55.1	55.6	0.4	7.7	445

FOR ELECTROWINNING, WHY THE IONWINNER?

- Designed for Lowest Operating Costs per pound of Copper.
  - Reusable 316 ss cathodes.
  - Combines Electrowinning and IX in one System.
    - Electrowinning of Concentrated Copper Only.
    - IX for Re-Concentration with no added chemicals.
    - Acid Reuse Design
    - Low, Low Copper in Discharge.
- Integrated Design for Plating Tools.
- Recovered Copper is 99.9+% Copper.

TYPICAL COSTS FOR ELECTROWINNING COPPER Per POUND OF COPPER

Cost Factors	ELECTRICITY	ANODES	CATHODES	LABOR	MISC.	TOTAL COST
Flat Plate with Scrap Board Cathodes	$ 0.26	$ 0.31	-	0.39	$ 0.17	$ 1.13
Flat Plate, 316SS Cathodes	$ 0.26	$ 0.31	$ 0.07	$ 0.78	$ 0.17	$ 1.59
Reticulate Cathode	$ 0.26	$ 0.31	$ 1.40	$ 0.39	$ 0.17	$ 2.53
Carbon Fiber Cathode	$ 0.26	$ 0.31	$ 10.00	$ 0.78	$ 0.17	$ 11.52
Barrel Cell	$ 0.67	$ 0.31	$ 0.50	$ 0.26	$ 0.17	$ 1.91

Value of copper recovered	$ 0.55
Sludge Disposal Cost Avoided at $300/Ton	$ 1.05