

I. INTRODUCTION

Enhancing the Co-Precipitation Process for Industrial Waste Metal Removal in a Continuous Reactor

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Abstract—A continuous copper precipitation treatment (CCPT) system was conceived at Intel Chandler Site to serve as a first-of-kind (FOK) facility-scale waste copper (Cu), nickel (Ni), and manganese (Mn) co-precipitation facility. The process was designed to treat highly variable wastewater discharged from a substrate packaging research factory. The paper discusses metals co-precipitation induced by internal changes for manufacturing facilities that lack the capacity for hardware expansion due to real estate restrictions, aggressive schedules, or budgetary constraints. Herein, operating parameters such as pH and oxidation reduction potential (ORP) were examined to analyze the ability of the CCPT System to immobilize various waste metals. Additionally, influential factors such as influent concentrations and retention times were investigated to quantify the environmental variability against system performance. A total of 2,027 samples were analyzed and statistically evaluated to measure the performance of CCPT that was internally retrofitted for Mn abatement to meet environmental regulations. In order to enhance the consistency of the influent, a separate holding tank was cannibalized from another system to collect and slow-feed the segregated Mn wastewater from the factory into CCPT. As a result, the baseline influent Mn decreased from $17.2 \pm 18.7 \text{ mg}^1\text{L}^{-1}$ at pre-pilot to $5.15 \pm 8.11 \text{ mg}^1\text{L}^{-1}$ post-pilot (70.1% reduction). Likewise, the pre-trial and post-trial average influent Cu values to CCPT were $52.0 \pm 54.6 \text{ mg}^1\text{L}^{-1}$ and $33.9 \pm 12.7 \text{ mg}^1\text{L}^{-1}$, respectively (34.8% reduction). However, the raw Ni content of $0.97 \pm 0.39 \text{ mg}^1\text{L}^{-1}$ at prepilot increased to $1.06 \pm 0.17 \text{ mg}^1\text{L}^{-1}$ at post-pilot. The average Mn output declined from $10.9 \pm 11.7 \text{ mg}^1\text{L}^{-1}$ at pre-pilot to $0.44 \pm 1.33 \text{ mg}^1\text{L}^{-1}$ at post-pilot (96.0% reduction) as a result of the pH and ORP operating setpoint changes. In similar fashion, the output Cu quality improved from $1.60 \pm 5.38 \text{ mg}^1\text{L}^{-1}$ to $0.55 \pm 1.02 \text{ mg}^1\text{L}^{-1}$ (65.6% reduction) while the Ni output sustained a 50% enhancement during the pilot study ($0.22 \pm 0.19 \text{ mg}^1\text{L}^{-1}$ reduced to $0.11 \pm 0.06 \text{ mg}^1\text{L}^{-1}$). pH and ORP were shown to be significantly instrumental to the precipitative versatility of the CCPT System.

H

EAVY metals in wastewater are typically present in complexed and non-complexed forms that require abatement prior to environmental discharge. There are a multitude of conventional treatment techniques applicable to heavy metals removal in the wastewater industry that utilizes physical, chemical, and biological processes. Examples of such methods have been benchmarked in industry and academia; including oxidation [10], adsorption [3], chemical precipitation [5], ion exchange [5], and electro-deposition [5].

A qualitative assessment of metals solubility is provided in detail to guide the audience in regard to the fundamentals of precipitation.

The treatability of Cu, Mn, and Ni via precipitation in waste abatement applications is directly related to their solubility in the solvent matrix. Their solubility profiles can be modified by one or more of the following process modifications: (1) manipulating the temperature of an aqueous solution [4], (2) adjusting the pH and reduction potential of the solution [8], or (3) super-saturation in a fixed-volume solution [11]. The concepts of pH and reduction potential are discussed further in this literature. Table I provides water solubility values and optimal pH values to describe the chemical precipitation hierarchy for various metals [2], [7].

TABLE I
WATER SOLUBILITIES OF METALS AT 25 °C (UNITS IN MG·L⁻¹)

| Metal | As Hydroxide | pH | As Sulfide | pH |
|-----------|----------------------|---------|-----------------------|----------|
| Cadmium | 2.3×10^{-5} | 10 - 11 | 6.7×10^{-10} | 8.5 - 10 |
| Chromium | 8.4×10^{-4} | 8 - 10 | No precipitate | - |
| Copper | 2.2×10^{-2} | 8 - 10 | 5.8×10^{-18} | 8 - 10 |
| Iron | 8.9×10^{-1} | 7 - 9 | 3.4×10^{-5} | 7 - 9 |
| Lead | 2.1 | 9 - 11 | 3.8×10^{-9} | 8 - 10 |
| Manganese | 1.2 | 9 - 11 | 2.1×10^{-3} | 9 - 11 |
| Nickel | 6.9×10^{-3} | 9 - 11 | 6.9×10^{-8} | 9 - 11 |
| Silver | 13.3 | 11 - 13 | 7.4×10^{-12} | 11 - 13 |
| Zinc | 1.10 | 9 - 11 | 2.3×10^{-7} | 8 - 10 |

pH is an indicator of hydrogen ion (H⁺) concentration and controls the molecular net electric charge of a known substance as a means to manipulate its mobility in the water matrix [2]. A metal with low mobility (insoluble) has a negative net charge (H⁺ depletion), which subsequently precipitates out of the liquid phase. This process usually occurs in high pH regions and is often referred to as alkaline precipitation. Contrariwise, a heavy metal with high



mobility (soluble) has a net positive charge as a result of H⁺ supplementation in solution, thus translating to aqueous dissolution of metals in acidic environments.

ORP is a measure of the potential for electron transfer, where the magnitude indicates the strength / degree of electron exchange and sign indicates oxidation (positive) and reduction (negative). ORP is measured by enumerating the voltage disparity between an active electrode in the solution and a known reference electrode with units of measurement typically recorded as volts (V) or millivolts (mV) [6]. A notable weakness of ORP measurements is that they are usually composite-based or non-exclusive. In the other words, they do not distinguish between compounds such as oxidants, surfactants, organics, reducing agents, hydrated metals, or chelated metals [6]. Furthermore, the transfer of electrons in a solution also necessitates the migration of hydrogen ions (H⁺), consequently signifying the sensitivity of ORP to pH variations [1]. Ideally, a conceivably adequate metals precipitation system with steady-state influent concentrations would achieve predetermined ORP operating setpoints that indicate the comprehensive neutralization of oxidation-reduction reactions in an electron-rich environment.

pH and ORP are minimally dependent on influent concentrations and residence times. However, their respective setpoints are holistically critical to controlling the dynamic states of the metals in undisturbed environments. As such, it is conceivable that changes in influent concentrations and residence times are direct indicators of deviations to the steady-state configuration of a treatment system.

II. RESEARCH OBJECTIVE

Intel Chandler developed a CCPT system that was initially designed to treat Cu and Ni wastewater discharged from a substrate packaging research factory. A series of process modifications were recently implemented to enable the system to precipitate Mn and concurrently preserve Cu and Ni abatement while still meeting environmental discharge regulations.

Using certain statistical elements that were inspired by the Seven Basic Tools of Quality [9], [12], this paper will specifically evaluate the removal of Mn before and after system modifications as a function of pH and ORP adjustments, influent concentration fluctuations, and system hydraulic residence times. Additionally, alterations to Cu and Ni output quality baselines were also investigated. Fig. 1 summarizes the root cause roadmap for CCPT quality output performance.

Fig. 1 Output Quality Cause-and-effect Fishbone Diagram

Since the process changes were only applied to subparts of the Method and Environment groups, the journal will not discuss impacts of the Machine, Man-power, Measurement, and Materials categories as their sub-components were unchanged throughout the pilot study. Additionally, the process mixing speed was constant and the treatment system operated indoors at room temperature. Although the system was heavily influenced by upstream manufacturing operations, those variations are captured in the influent concentration and flow impact assessment scopes of this pilot study.

III. MATERIALS AND METHODS

A. Influent Wastewater Profile

The influent wastewater profile recorded at the initiation of the pilot study is summarized in Table II.

TABLE II
INFLUENT WASTEWATER PROFILE (UNITS IN MG³L⁻¹)

| Constituent | Low | Average | Deviation | Median | High |
|-------------|------|---------|-----------|--------|------|
| Cu | 0.10 | 52.0 | 54.6 | 40.9 | 697 |
| Ni | 0.10 | 0.97 | 0.39 | 0.94 | 4.97 |
| Mn | 0.10 | 17.2 | 18.7 | 14.9 | 208 |

B. Pre-Pilot Treatment System Materials and Operation

The pilot study was executed on a CCPT system that was designed to treat between 200 mg³L⁻¹ and 1,000 mg³L⁻¹ raw Cu. Fig. 2 illustrates the process flow diagram (PFD) for the treatment system.

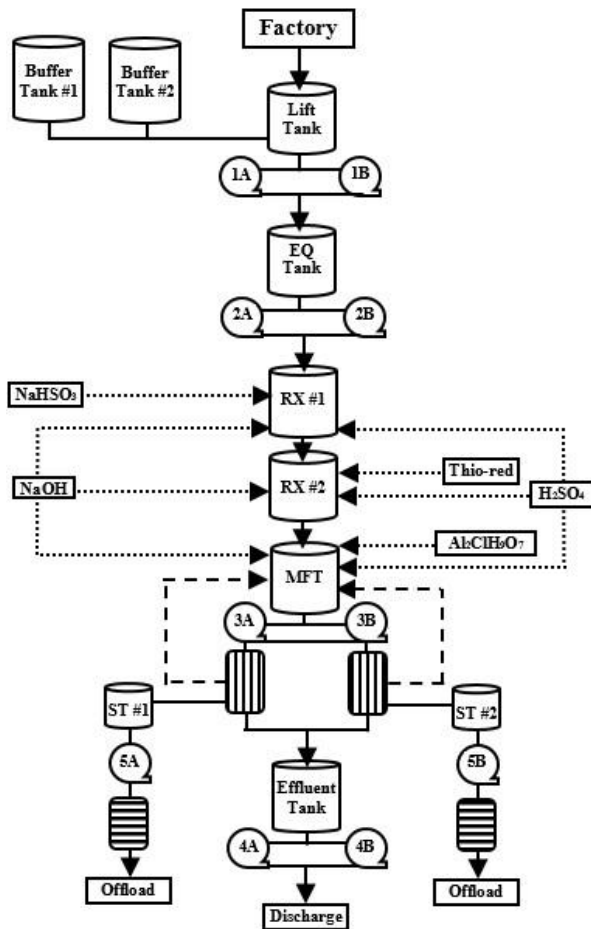


Fig. 2 CCPT Pre-pilot Process Flow Diagram

The intent of the lift and buffer tanks was to collect and standardize the hydraulic loading from the factory to accommodate the downstream cascade flow configuration of the treatment system. Reactor #1 was tasked with homogenizing the influent waste stream (dissolution of solids, uniformity of oxidation-reduction reactions, etc.) using setpoints defined in Table III. The normalized waste stream was then immediately exposed to hydroxides and sulfides in Reactor #2. This procedure was significantly imperative to the health of the treatment system by initiating the precipitation of the aqueous waste metals. The stream was then conveyed into the Microfilter Feed Tank (MFT), where aluminum is introduced as a polishing agent to preserve and promote supplemental metals co-precipitation in an alkaline environment. The downstream microfilters continuously recirculated the waste stream back to the MFT and used pressurized filtration to collect the precipitated metals. The microfilters were procured from Duraflow (Model DF-415 Polyvinylidene Fluoride Membranes) with a pore size between 0.1 and 0.2 μm . The permeate flow from the microfilters was then transferred to the effluent tank for equalization and process monitoring prior to discharge. The condensed metals sludge was

conveyed to sludge thickeners (STs) for further sedimentation and decanting. The decant liquid was transferred back to the front end of the treatment system for re-treatment. Lastly, the remaining solids in the STs underwent pressurized compaction and dehydration in the filter presses (FPs) prior to third party offloading. With the exception of ST pumps, all other pumps used in this study were centrifugal, supplied with redundancy, and employed proportional-integral-derivative (PID) control loops to manage the liquid levels of their corresponding upstream tanks. The ST pumps were air-operated double diaphragms (AODDs) and manually operated by system operators. The pre-pilot unit operating setpoints for the CCPT system components are provided in Tables III-V.

TABLE III
CCPT PRE-PILOT UNIT OPERATIONS PROFILE

| Module ID | Function | Design | SP _{TWVa} | SP _{pHb} | SP _{ORPc} |
|------------|--------------------|-----------|--------------------|-------------------|--------------------|
| Lift Tank | Collect / Transfer | 1,500 gal | 35% | - | - |
| Buffer #1 | Alleviation | 4,000 gal | 100% | - | - |
| Buffer #2 | Alleviation | 4,000 gal | 100% | - | - |
| EQ Tank | Equalization | 5,242 gal | 70% | - | - |
| Reactor #1 | Homogenization | 3,343 gal | 90% | 4.5 | +205 mV |
| Reactor #2 | Precipitation | 3,343 gal | 75% | 8.5 | -205 mV |
| MFT | Microfilter Feed | 3,411 gal | 70% | 8.5 | -205 mV |
| MF #1 | Microfiltration | 15 gpm | - | - | - |
| MF #2 | Microfiltration | 15 gpm | - | - | - |
| Eff Tank | Process Monitor | 2,000 gal | 50% | - | - |

^aSP_{TWV} = operating setpoint for tank level working volume

^bSP_{pH} = operating setpoint for tank pH

^cSP_{ORP} = operating setpoint for tank ORP

In order to minimize the impacts of hydraulic shock loadings to the reactors, a separate PID control loop was implemented on Pumps 1A and 2A to limit the treatment system feed rate to minimum and maximum input flows of 12 and 35 gallons per minute (gpm), respectively. All excess flows sustained from the factory was diverted to an off-spec tank for subsequent peak-shaving operations.

TABLE IV CCPT SLUDGE
MANAGEMENT OPERATIONS PROFILE

| Module ID | Function | Design | SP _{TWVa} | SP _{psib} |
|-----------|---------------|--------------------|--------------------|--------------------|
| ST #1 | Sedimentation | 2,000 gal | variable | - |
| ST #2 | Sedimentation | 2,000 gal | variable | - |
| FP #1 | Densification | 35 ft ³ | - | 3,000 psi |
| FP #2 | Densification | 35 ft ³ | - | 3,000 psi |

^aSP_{TWV} = operating setpoint for tank level working volume

^bSP_{psi} = operating pressure setpoint for filter press

TABLE V
CCPT WASTE CONVEYANCE UNIT OPERATIONS

| Module ID | Function | Design | Manufacturer and Series |
|-----------|-------------------|--------------------|--------------------------|
| Pump 1A | Transfer to EQ | 100 gpm | - |
| Pump 1B | Transfer to EQ | 100 gpm | - |
| Pump 2A | Reactor #1 Feed | 75 gpm | Finish Thompson UC1516 |
| Pump 2B | Reactor #1 Feed | 75 gpm | Finish Thompson UC1516 |
| Pump 3A | MF #1 Recirculate | 350 gpm | Grundfos CR90-2-1-H |
| Pump 3B | MF #2 Recirculate | 350 gpm | Grundfos CR90-2-1-H |
| Pump 4A | Final Discharge | 120 gpm | Finish Thompson UC1516 |
| Pump 4B | Final Discharge | 120 gpm | Finish Thompson UC1516 |
| Pump 5A | Transfer to FP | 50 gpm | Ingersoll Rand PD30A |
| Pump 5B | Transfer to FP | 50 gpm | Ingersoll Rand PD30A |
| FP #1 | Filter Press #1 | 35 ft ³ | Siemens 1200G32-2735SYLC |
| FP #2 | Filter Press #2 | 35 ft ³ | Siemens 1200G32-2735SYLC |

C. Post-Pilot Treatment System Materials and Operation

Throughout the pilot study, pH and ORP setpoint changes were performed to precipitate Mn. Lastly, a dedicated holding tank was used to segregate the Mn wastewater and bleed into the EQ Tank. Table VI summarizes the post-pilot precipitation unit operating setpoints, while Fig. 3 illustrates the CCPT System physical hardware modifications.

TABLE VI CCPT POST-PILOT UNIT OPERATIONS PROFILE

| Module ID | Function | Design | SP _{TWVa} | SP _{pHb} | SP _{ORPc} |
|------------|--------------------|------------|--------------------|-------------------|--------------------|
| Lift Tank | Collect / Transfer | 1,500 gal | 35% | - | - |
| Buffer #1 | Alleviation | 4,000 gal | 100% | - | - |
| Buffer #2 | Alleviation | 4,000 gal | 100% | - | - |
| EQ Tank | Equalization | 5,242 gal | 70% | - | - |
| Mn Tank | Mn Segregation | 25,000 gal | 20% | - | - |
| Reactor #1 | Homogenization | 3,343 gal | 90% | 2 | +205 mV |
| Reactor #2 | Precipitation | 3,343 gal | 75% | 10.5 | -476 mV |
| MFT | Microfilter Feed | 3,411 gal | 70% | 10.5 | +55 mV |
| MF #1 | Microfiltration | 15 gpm | - | - | - |
| MF #2 | Microfiltration | 15 gpm | - | - | - |
| Eff Tank | Process Monitor | 2,000 gal | 50% | - | - |

^a SP_{TWV} = operating setpoint for tank level working volume

^b SP_{pH} = operating setpoint for tank pH

^c SP_{ORP} = operating setpoint for tank ORP

The addition of the Mn EQ Tank was intended to segregate the Mn wastewater (5,000 – 10,000 gallons weekly) from the collection system for hydraulic attenuation during factory maintenance activities. When the maintenance efforts were completed, the stream was re-introduced into the treatment system over a period between

12 and 24 hours, depending on field conditions. The pH and ORP setpoints were changed to precipitate Mn from the waste stream while preserving the existing capacity to immobilize the Cu and Ni in the system.

E. Sampling and Wet Chemistry Metrology

Sample collection was conducted at the EQ Tank and Effluent Tank using two automated ISCO Samplers (Teledyne ISCO Model 6712). One sampler was located at the equalization tank upstream of the first reactor, while the other sampler was placed in the effluent tank downstream of the microfiltration unit. Each sampler pulled 80 mL of fresh liquid per 40 minutes to be compiled into 4-hour composites on a daily basis. This method translated to a daily regimen of six influent samples and six effluent samples, each representing 4-hour concentration averages over a 24-hr period.

The samples were acidified with nitric acid (HNO₃) and filtered through a 0.45 μm filter prior to undergoing inductively coupled plasma optical emissions spectrometry (ICP-OES). The minimum analytical resolution for the ICPOES instrument was 0.10 mg¹L⁻¹ for Cu, Ni, and Mn.

F. Treatment System Monitoring Instrumentation

Treatment system operating pH values were recorded using redundant George Fischer Signet 2722 pH Sensors. ORP values were also recorded using redundant George Fischer Signet 2724 ORP Sensors. Influent flow measurements were obtained using a George Fischer Signet 2551 Magmeter Flow Transmitter at the EQ Tank. All sensor data were collected in real-time and uplinked to Facilities Monitoring System (FMS) for subsequent data extraction from the Supervisory Control and Data Acquisition (SCADA) repository on an as-needed basis. All instrumentation data were compiled into 4-hr composites to align with the wastewater sampling methodology.

G. System Performance Equations and Denotations

The influent flow measurements to the treatment system were recorded at the EQ Tank pumps and used to calculate the critical HRT:

$$HRT_{4\text{-hr, critical}} = [\sum(V_{\text{reactor}} \times SP_{TWV}) / Q_{\text{flow, 4-hr critical}}] \quad (1)$$

where HRT_{4-hr, critical} is the 4-hr average critical hydraulic residence time (HRT) in minutes, Q_{flow, 4-hr, critical} is the 4-hr composite critical feed flowrate from the EQ Tank recorded as gpm, V_{reactor} is the fixed design volume of each reactor, and SP_{TWV} is the fixed reactor setpoint tank level working volume (%) from Table II. Since each reactor used different working volumes, the critical HRT of the CCPT was

comprised of the collective retention times in Reactor #1, Reactor #2, and MFT.

Other performance parameter denotations were generated to label the 4-hr composite critical pH reading ($pH_{critical, 4-hr}$), the 4-hr composite critical ORP reading in mV ($ORP_{critical, 4-hr}$), the 4-hr composite influent metal concentration in mg^1L^{-1} ($[Influent]_{4-hr}$), and the 4-hr composite effluent metal concentration in mg^1L^{-1} ($[Effluent]_{4-hr}$).

H. Statistical Process Analyses (SPA) Methodology

Performance data pertaining to CCPT were sequestered into 90-day increments to enable extensive evaluation of the implemented process changes. Scatter plots were generated to illustrate the relationship between the input variables and response variables. To compare output quality against the various elements of system behavior, the $[Effluent]_{4-hr}$ values for Cu, Mn, and Ni are identified as the response variables.

Process parameters such as $[Influent]_{4-hr}$, pH_{4-hr} , $HRT_{critical, 4-hr}$, and ORP_{4-hr} were identified as the input variables.

The computations used to generate the 90-day statistical valuations are as follows:

$$\bar{X}_{90-day} = [1 / N_{DP, 90 days}] \sum DP, 90 days \tag{2}$$

$$\sigma_{90-day} = [\sum_{90 days} (DP - \bar{X}_{90-day})^2 / N_{DP, 90 days} - 1]^{0.5} \tag{3}$$

$$LSL_{90-day} = [\bar{X}_{90-day} - (2 \times \sigma_{90-day})] \tag{4}$$

$$USL_{90-day} = [\bar{X}_{90-day} + (2 \times \sigma_{90-day})] \tag{5}$$

$$LCL_{90-day} = [\bar{X}_{90-day} - (3 \times \sigma_{90-day})] \tag{6}$$

$$UCL_{90-day} = [\bar{X}_{90-day} + (3 \times \sigma_{90-day})] \tag{7}$$

$$Range_{90-day} = High_{90-day} - Low_{90-day} \tag{8}$$

where \bar{X}_{90-day} is the 90-day average, $N_{DP, 90 days}$ is the number of data points in the 90-day period, and $\sum DP, 90 days$ is the sum of the data points in the 90-day period. The σ_{90-day} is the 90-day standard deviation, $\sum_{90 days} (DP - \bar{X}_{90-day})$ is the sum of the differences between the 90-day average and each data point in the same 90-day period. LSL_{90-day} and USL_{90-day} are the corresponding 90-day lower and upper specification limits.

LCL_{90-day} and UCL_{90-day} are the 90-day lower and upper control

limits, respectively. The $Range_{90-day}$ is the 90-day difference between the maximum and minimum values of the corresponding 90-day data set.

Each 90-day impact assessment provided herein was accompanied by a control limit residency (CLR) evaluation to determine the proportion of data samples that reside under the upper control limits of the response variables and within the control limits of the input variables. This procedure compared the packing of the data points under the response variable UCLs with respect to the statistical migration of the input variable LCLs and UCLs at the conclusion of an induced system change.

IV. RESULTS AND DISCUSSION

A. Impact of Pilot Study on Influent Concentrations

Table VII synthesizes the 90-day influent metal profiles before and after the pilot study at the CCPT System.

TABLE VII
90-DAY INFLUENT BASELINE SUMMARY (UNITS IN MG^1L^{-1})

| Phase | Metal | Average | Median | σ | USL | UCL | High |
|------------|-------|---------|--------|----------|------|------|------|
| Pre-pilot | Cu | 52.0 | 40.9 | 54.6 | 161 | 216 | 697 |
| Post-pilot | Cu | 33.9 | 31.5 | 12.7 | 59.4 | 72.1 | 129 |
| Pre-pilot | Ni | 0.97 | 0.94 | 0.39 | 1.76 | 2.15 | 4.97 |
| Post-pilot | Ni | 1.06 | 1.00 | 0.17 | 1.40 | 1.57 | 2.38 |
| Pre-pilot | Mn | 17.2 | 14.9 | 18.7 | 54.7 | 73.4 | 208 |
| Post-pilot | Mn | 5.15 | 2.89 | 8.11 | 21.4 | 29.5 | 100 |

The average Mn influent dropped by 70.1% throughout the course of the pilot study. Subsequently, the influent Mn USLs and UCLs decreased by 60.9% and 59.8%, respectively. This particular milestone was alluded to the segregation of the Mn wastewater and the successive re-entry to the treatment system at a controlled feed rate. Likewise, the average, USL, and UCL values for influent Cu were also reduced by 34.8%,

63.1% and 66.6%, respectively. Moreover, the high values for all influent metals declined substantially, most particularly the Cu influent (81.5% reduction). Lastly, the standard deviation for influent Cu, Ni, and Mn decreased by 76.7%, 56.4%, and 56.7%, respectively, further implying a statistically progressive steady-state raw wastewater feed to the treatment system.

B. Overall Improvements to Metals Output

Tables VIII and IX summarize the pre-pilot and post-pilot effluent profiles for CCPT, which were compared to daily performance specification (p-spec) values for each metal.

TABLE VIII
PRE-PILOT 90-DAY BASELINE EFFLUENT (UNITS IN MG^1L^{-1})

| Constituent | Average | Median | USL | UCL | High | P-spec |
|-------------|---------|--------|------|------|------|--------|
| Cu | 1.60 | 0.36 | 12.4 | 17.7 | 55.0 | 2.70 |
| Ni | 0.22 | 0.16 | 0.61 | 0.80 | 1.66 | 1.00 |

| | | | | | | |
|----|------|------|------|------|-----|------|
| Mn | 10.9 | 9.87 | 34.2 | 45.9 | 139 | 8.30 |
|----|------|------|------|------|-----|------|

TABLE IX

| POST-PILOT 90-DAY BASELINE EFFLUENT (UNITS IN MG ³ L ⁻¹) | | | | | | |
|---|---------|--------|------|------|------|--------|
| Constituent | Average | Median | USL | UCL | High | P-spec |
| Cu | 0.55 | 0.25 | 2.59 | 3.61 | 11.4 | 2.70 |
| Ni | 0.11 | 0.10 | 0.24 | 0.30 | 0.89 | 1.00 |
| Mn | 0.44 | 0.10 | 3.09 | 4.42 | 16.2 | 8.30 |

The pilot study modifications were shown to enhance the CCPT process capability for metals co-precipitation. The average Mn output dropped by 96.0%. Hence, the Mn USLs and UCLs decreased by 91.0% and 90.4%, respectively, to fall below the pre-determined p-spec of 8.30 mg³L⁻¹. The average, USL, and UCL values for Cu were also reduced by 65.6%, 79.1% and 79.6%, respectively. However, the Cu SPC limits did not drop to below the daily p-spec of 2.70 mg³L⁻¹. Although the output Ni USLs and UCLs improved by 60.7% and 62.5%, respectively, they were initially below the Ni pspec of 1.00 mg³L⁻¹ prior to the start of the pilot study. Lastly, the high values for all metals were significantly reduced, most notably Mn output (84.0% decline), further validating the statistical improvement of the pilot study notwithstanding the introduction of the new Mn waste stream to the system.

C. Impact of pH on Metals Output

The first step in the metals immobilization process was hydroxide precipitation in Reactor #2. The pH setpoints for Reactor #2 and the MFT were consistently identical during the pilot study. Hence, the pH values recorded in the MFT functioned as the critical pH for CCPT. The comparisons of effluent metals to the critical pH are shown in Figs. 4-6.

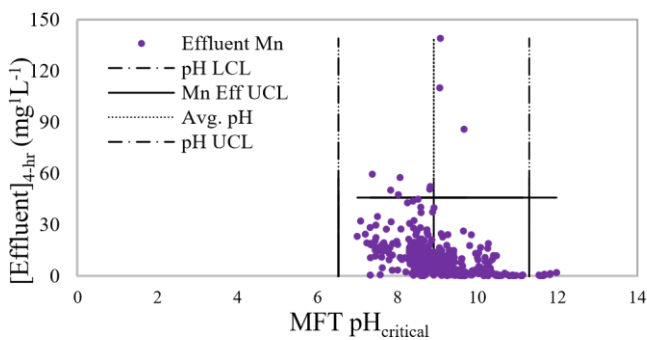
The pre-pilot scatter plots for critical pH vs. Effluent Concentrations for Ni and Mn show a slightly low negative correlation, indicating that alkaline precipitation is insufficient at a range between the pH LCL and pH average. However, this deduction inversely applies to effluent Cu, which is optimal in the same region. Contrariwise to the Ni and Mn profiles, the pre-pilot effluent Cu increases with respect to pH values exceeding the pH UCL, thus alluding to the re-mobilization of Cu in extreme pH conditions.

Table X shows a considerable compaction of the pH control limit range before and after the pilot study, 4.78 units at prepilot reduced to 1.33 units at post-pilot (72.2% contraction). Additionally, the operating pH setpoint increased by a full 2 units (23.5% increase). Concurrently, Table XI shows at least 94.7% of the post-pilot effluent metals sampling data resided under the reduced effluent UCLs and within the newly compressed pH control limits. It is likely that the pH setpoint changes contributed to the improved metals effluent quality.

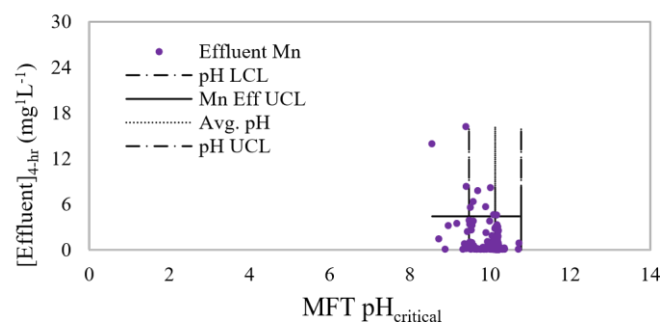
(a)

(b)

Fig. 5 Critical pH vs. Effluent Ni Concentration (a) pre-pilot study and (b) post-pilot study



(a)



(b)

Fig. 6 Critical pH vs. Effluent Mn Concentration (a) pre-pilot study and (b) post-pilot study

TABLE X

| CRITICAL 4-HR COMPOSITE PH PROFILE | | | | | | |
|------------------------------------|-----|-----|---------|-----|------|----------|
| Phase | Low | LCL | Average | UCL | High | Setpoint |

| | | | | | | |
|------------|------|------|------|------|------|------|
| Pre-pilot | 7.08 | 6.52 | 8.91 | 11.3 | 12.0 | 8.50 |
| Post-pilot | 8.55 | 9.47 | 10.1 | 10.8 | 10.7 | 10.5 |

TABLE XI

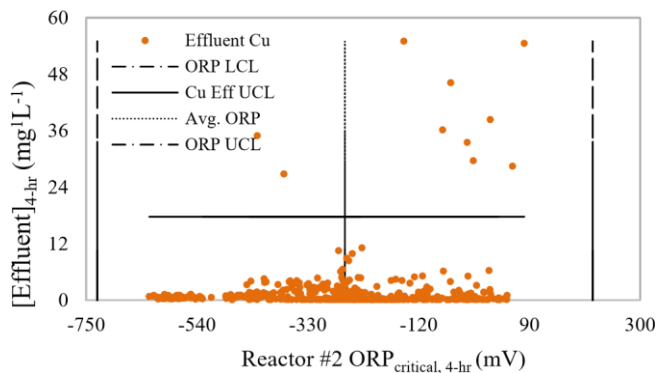
PH-INDUCED 90-DAY EFFLUENT CLR EVALUATION SUMMARY

| Phase | Metal | # samples | # CLR | % CLR | UCL (mg ^l L ⁻¹) |
|------------|-------|-----------|-------|-------|--|
| Pre-pilot | Cu | 548 | 528 | 96.4% | 17.7 |
| Post-pilot | Cu | 526 | 498 | 94.7% | 3.61 |
| Pre-pilot | Ni | 548 | 519 | 94.7% | 0.80 |
| Post-pilot | Ni | 526 | 498 | 94.7% | 0.30 |
| Pre-pilot | Mn | 548 | 529 | 96.5% | 45.9 |
| Post-pilot | Mn | 526 | 500 | 95.1% | 4.42 |

D. Impact of Critical ORP on Metals Output

The waste metals were first exposed to sulfide precipitants in Reactor #2. Hence, the ORP values recorded in Reactor #2 provided the critical ORP for CCPT. The comparisons of effluent metals to the ORP values in Reactor #2 are illustrated in Figs. 7-9.

The scatter plots for critical ORP vs. Effluent Concentration for all metals show a persistently low-volume residency of effluent UCL outliers in elevated ORP regions. These faintly



low positive correlations suggest that sulfide precipitation was not optimal at these ranges and additional sulfur reagents were needed complete the metals immobilization process in Reactor #2. Despite the

(a)

significant compaction of the ORP LCL and UCL values on the post-pilot scatter plots, the low positive relationships are nonetheless verified at an even lower magnitude and further expounds the importance of ORP control during system operations.

TABLE XII

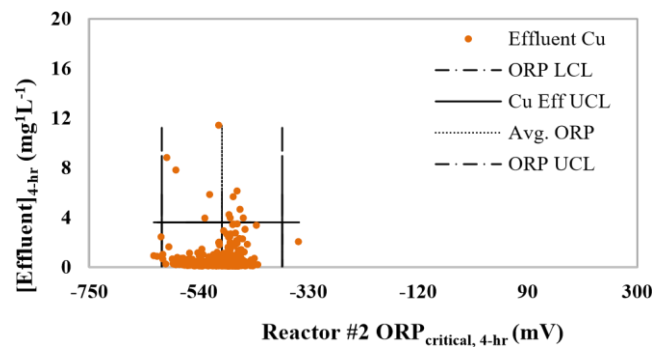
CRITICAL 4-HR COMPOSITE ORP PROFILE (UNITS IN MV)

| Phase | Low | LCL | Average | UCL | High | Setpoint |
|------------|------|------|---------|------|------|----------|
| Pre-pilot | -631 | -729 | -260 | 210 | 80.3 | -205 |
| Post-pilot | -626 | -611 | -496 | -380 | -349 | -476 |

TABLE XIII

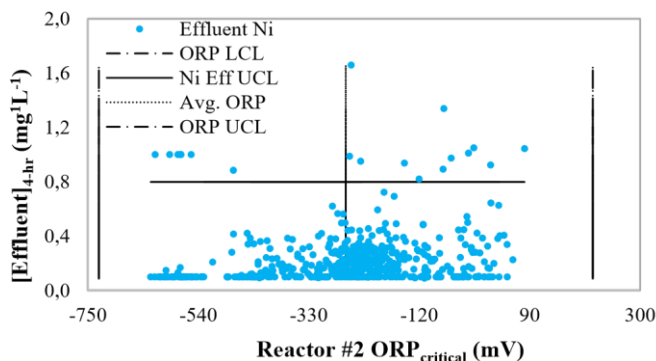
ORP-INDUCED 90-DAY EFFLUENT CLR EVALUATION SUMMARY

| Phase | Metal | # samples | # CLR | % CLR | UCL (mg ^l L ⁻¹) |
|------------|-------|-----------|-------|-------|--|
| Pre-pilot | Cu | 548 | 538 | 98.2% | 17.7 |
| Post-pilot | Cu | 526 | 508 | 96.6% | 3.61 |
| Pre-pilot | Ni | 548 | 529 | 96.5% | 0.80 |
| Post-pilot | Ni | 526 | 510 | 97.0% | 0.30 |
| Pre-pilot | Mn | 548 | 539 | 98.4% | 45.9 |
| Post-pilot | Mn | 526 | 511 | 97.2% | 4.42 |

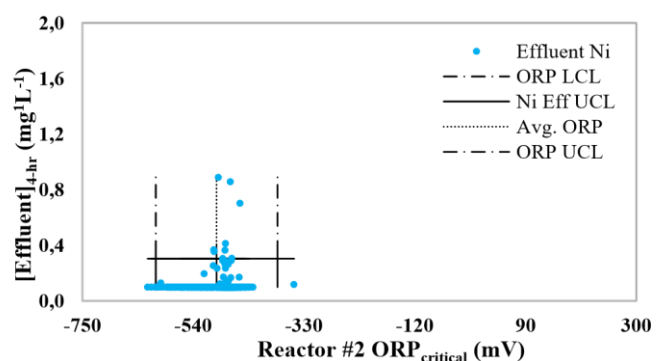


(b)

Fig. 7 Critical ORP vs. Effluent Cu Concentration (a) pre-pilot study and (b) post-pilot study

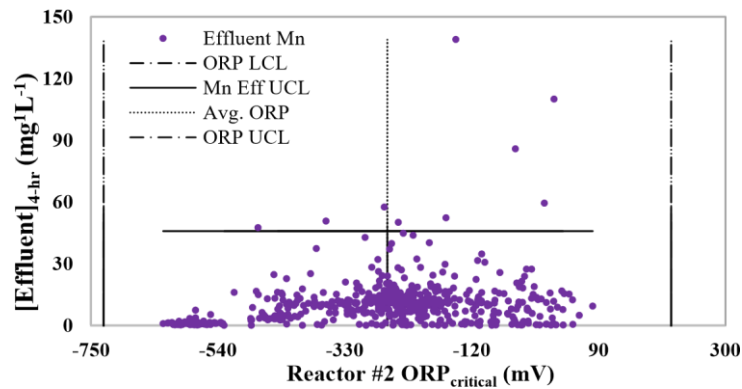


(a)

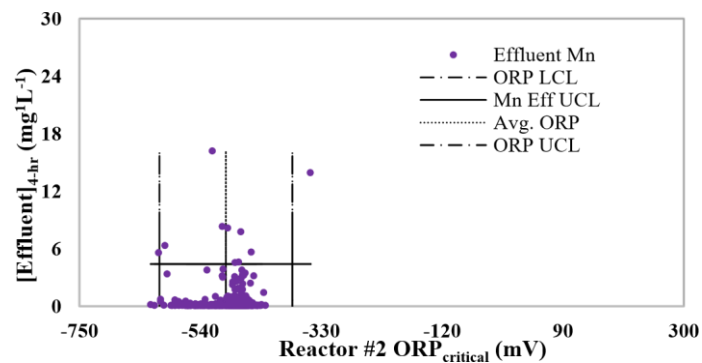


(b)

Fig. 8 Critical ORP vs. Effluent Ni Concentration (a) pre-pilot study and (b) post-pilot study



(a)



(b)

Fig. 9 Critical ORP vs. Effluent Mn Concentration (a) pre-pilot study and (b) post-pilot study

Table XII discloses a substantial contraction of the ORP control limit range before and after the pilot study. The prepilot ORP control limit range at 939 mV was reduced to 231 mV (75.4% shrinkage) at the conclusion of the pilot study, which was triggered by a decrease in ORP operating setpoint of 271 mV (32.2% drop). Table XIII displays that a minimum 96.6% of the post-pilot effluent metals sampling data simultaneously resided under the diminished effluent UCLs and within the freshly compressed ORP control limits. Similar to the deduction derived from the critical pH, it is conceivable that the ORP setpoint changes improved the metals effluent quality.

E. Impact of Residence Time on Metals Output

Figs. 10-12 summarize the scatter plots that compare critical HRT to effluent metals at the CCPT System.

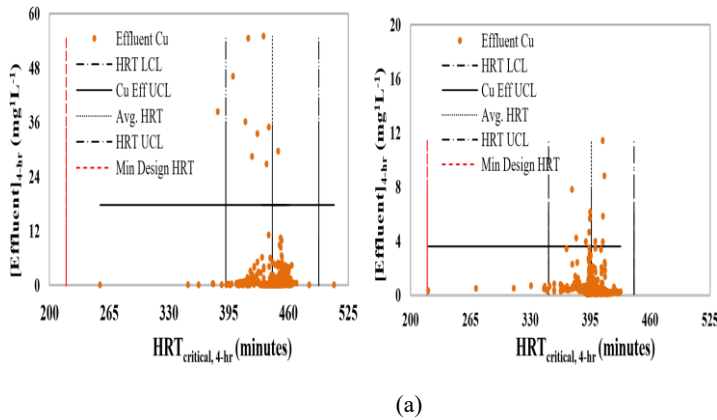


Fig. 10 Critical HRT vs. Effluent Cu Concentration (a) pre-pilot study and (b) post-pilot study

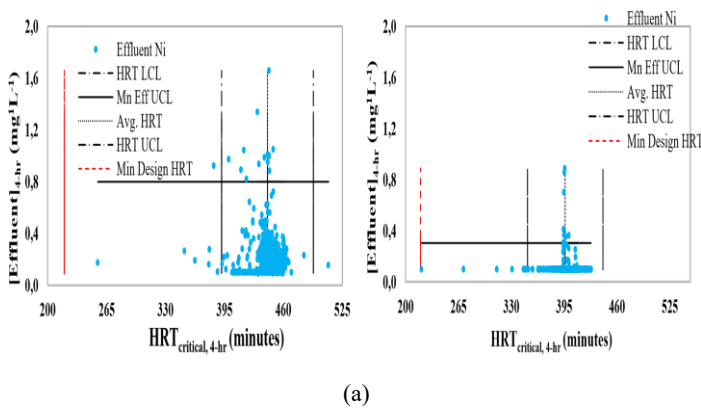


Fig. 11 Critical HRT vs. Effluent Ni Concentration (a) pre-pilot study and (b) post-pilot study

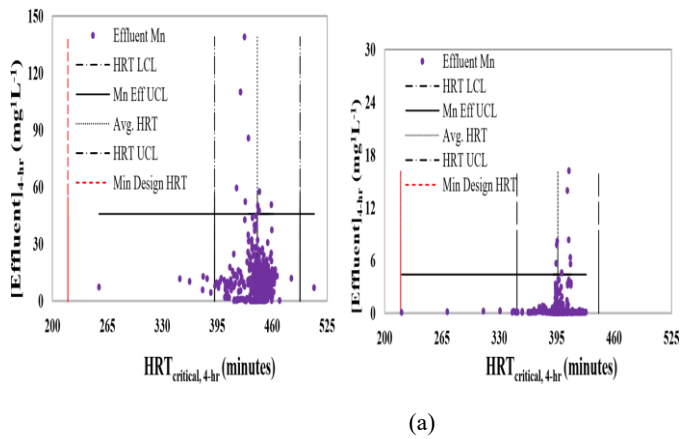


Fig. 12 Critical HRT vs. Effluent Mn Concentration (a) pre-pilot study and (b) post-pilot study

TABLE XIV

CRITICAL 4-HR COMPOSITE HRT PROFILE (UNITS IN MINUTES)

| Phase | Low | LCL | Average | UCL | High | Low Design |
|------------|-----|-----|---------|-----|------|------------|
| Pre-pilot | 255 | 392 | 442 | 493 | 510 | 218 |
| Post-pilot | 218 | 350 | 396 | 443 | 428 | 218 |

Table XV shows that on the back-end of the pilot study, at least 95.8% of the effluent metals sample data resided below their respective UCLs and within the LCL and UCL of the

$HRT_{critical, 4-hr}$, which is up 0.9% from the minimum 94.9% observed at the start of the study. Table XIV reveals that the pre-pilot and post-pilot operating ranges for $HRT_{critical, 4-hr}$ were 255 minutes and 210 minutes, respectively. In essence, the 17.6% compression in retention time operating range did not adversely impact the improved quality profile for all effluent metals at the conclusion of the project.

TABLE XV

| HRT-INDUCED 90-DAY EFFLUENT CLR EVALUATION SUMMARY | | | | | |
|--|-------|-----------|-------|-------|--|
| Phase | Metal | # samples | # CLR | % CLR | UCL (mg ¹ L ⁻¹) |
| Pre-pilot | Cu | 548 | 529 | 96.5% | 17.7 |
| Post-pilot | Cu | 526 | 504 | 95.8% | 3.61 |
| Pre-pilot | Ni | 548 | 520 | 94.9% | 0.80 |
| Post-pilot | Ni | 526 | 506 | 96.2% | 0.30 |
| Pre-pilot | Mn | 548 | 529 | 96.5% | 45.9 |
| Post-pilot | Mn | 526 | 505 | 96.0% | 4.42 |

V. CONCLUSION

A. Review

The reduction in average, specification limit, and control limit effluent values for all metals during the CCPT pilot study alluded to a holistically improved co-precipitation performance profile. The segregation of the Mn wastewater and re-entry into the treatment system was ensued by the enhanced stability of the Mn influent, thus reducing the influent variability imposed by upstream factory operations. The changes to pH and ORP operating setpoints significantly enhanced Mn output quality to meet performance specifications while also improving the Cu and Ni abatement performance baseline. The hydraulic retention time was determined to be minimally impactful on the effluent quality of the waste metals from the treatment system.

B. Comments and Recommendations for Future Work

Referring to Fig. 1, the literature proposes to expand on the cause-and-effect evaluation of the CCPT performance with regards to elements of the Materials, Measurement, Manpower, and Machine categories. While the Method and Environment components of treatment system are currently sufficient for metals co-precipitation, an extensive diagnosis of system performance influenced by hardware maintenance, human input variability, online metrology excursions, equipment failures, material impurities, and process control loop automation would expose common cause and special cause malfunctions of the system. The results acquired from this statistical failure mode engineering assessment (FMEA) would identify additional opportunities for system optimization and standardize a robust design specification for future systems of similar

functionality. Additionally, alternative process control methods such as metrology-induced chemical dosing algorithms (reduce or eliminate ORP process control), treatment process chemical substitutions, and installing variable frequency drive (VFD) chemical delivery systems would further optimize system performance while reducing process chemical demand.

In addition to understanding the various failure modes of the treatment system, a waste byproduct analysis would assist in comprehending the environmental side effects of CCPT. The results would trigger an investigation into evaluating alternative process chemicals for treatment, thus alleviating the environmental footprint of the system and potentially adding value to the waste byproducts.

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