

Heavy Metals Removal

Enhancing the Co-Precipitation Process for Heavy Metal Industrial Waste Treatment

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Co-precipitation gains ground as a popular cost-effective alternative to conventional treatment of industrial wastewater (Parts 1 & II Environmental Technology Journal, January to April 1999)

Wastewater from industrial processes such as electroplating, painting, degreasing, and engine testing and maintenance activities typically contain heavy metals that must be removed prior to discharge in order to meet NPDES requirements. Although several technologies are available for heavy metals treatment, many of these systems employ treatment techniques that are not cost effective. An innovative technology that uses a process known as co-precipitation has been increasingly recognized as an alternative to conventional treatment of industrial waste waters, resulting in significant cost benefits to plant owners and operators.

Co-precipitation occurs when ferrous iron is added to metallic waste streams and subsequently oxidized in an aerated reactor. The oxidized iron, which is insoluble, precipitates along with other metallic contaminants present in the waste stream, thereby enhancing metals removal. The precipitates can then be separated from the treated water by chemical coagulation, flocculation and clarification processes. The clarified effluent is subsequently filtered to remove any residual solids prior to discharge.

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Background

Science Applications International Corporation (SAIC) recently designed and installed a 1,460 gpm metals treatment process to replace the insoluble sulfide precipitation processes which were being used for industrial wastewater treatment of an aircraft maintenance facility in Texas. This metals treatment system consisted of two 700 gpm co-precipitation units and one 60 gpm co-precipitation pretreatment unit (Figure 1). The design incorporated the co-precipitation process and equipment developed by Unipure Environmental, Fullerton, California.



Figure 1. Co-precipitation system (1-60 gpm and 2-700 gpm) installed by SAIC

The design treatment standards (design criteria) were based on the limits established for the facility under its National Pollutant Discharge Elimination System (NPDES) and Texas Natural Resource Conservation Commission (TNRCC) permits. SAIC then conducted an optimization study to minimize the consumption of process chemicals (e.g., ferrous chloride, sodium hydroxide, and anionic polymer) while maximizing metals

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removal. Influent characteristics for the optimization study are shown on Table 1 and Figure 2.

Co-precipitation Process Overview

The primary processes used by the co-precipitation metals treatment system are co-precipitation, coagulation, and flocculation (Figure 3). The process utilizes three main

Table 1. Co-precipitation system influent/effluent concentrations vs permit limits

| LOCATION | Monitored Parameters/Results (mg/L) | | | | |
|------------------------------------|-------------------------------------|--------|-------|-------|-------|
| | Cd | Cr | Cu | Ni | Zn |
| Influent | 0.067 | 60.962 | 0.089 | 26.6 | 0.441 |
| Effluent | 0.01 | 0.116 | 0.01 | 0.406 | 0.05 |
| Discharge Std Permit (Single Grab) | 1.2 | 7 | 4.5 | 4.1 | 4.2 |

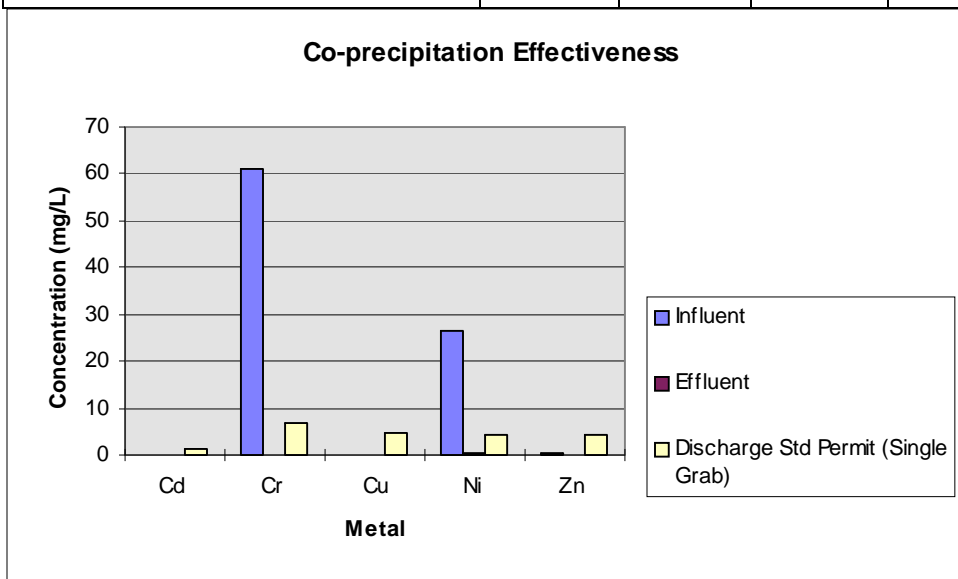


Figure 2. Co-precipitation system influent/effluent concentrations vs permit limits

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components: a reactor, a chemical mix chamber and a lamella-plate clarifier. A ferrous chloride (11 percent by volume) solution is injected into the influent waste stream prior to the reactor which is used for precipitation of the heavy metals. Sodium hydroxide is used to maintain the pH in the reactor at 7.5 - 8.0. Air is introduced into the reactor to

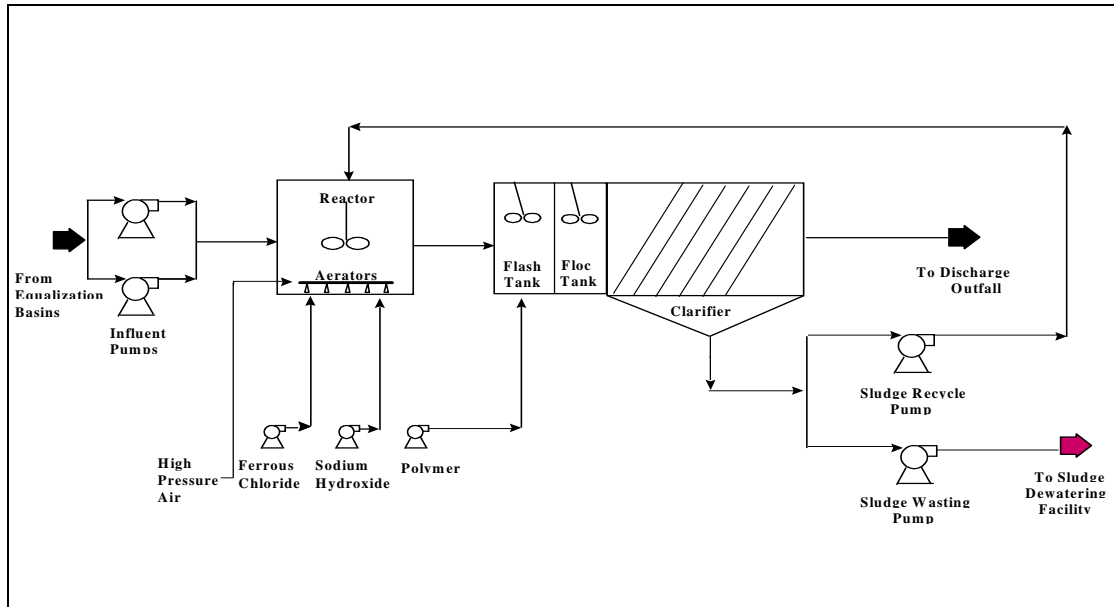


Figure 3. Co-precipitation metals treatment process flow diagram

oxidize the ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}). Ferric iron precipitates and entraps heavy metals into its matrix. Ferric iron further acts as a catalyst for oxidation of the remaining ferrous iron to ferric iron. The resulting solids laden water (ferric iron and the entrapped heavy metals) flows to the flash mix chamber. In the flash mix chamber of the clarifier an anionic polymer (50 percent by volume) is added to react with the solids to aid in the agglomeration of solids to form large particle sizes that will settle to the bottom of the clarifier. Some of the solids from the clarifier are recycled to the reactor to aid in the nucleation of metal precipitation.

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Treatment Benefits

The quantity of chemicals associated with the former sulfide precipitation waste treatment process is presented in Figure 4. Prior to the installation and implementation of the co-precipitation process, chemical use (ferrous sulfate, ferrous chloride, anionic polymer and sodium hydroxide) approximated 210,000 pounds per month for metals treatment at the facility. Most of the chemicals were consumed in the ferrous sulfide batching process. Since the installation of the co-precipitation process, a marked reduction in chemical consumption has been observed. In the six month period immediately following initiation of the co-precipitation process, chemical consumption was reduced to approximately 70,000 pounds per month; a reduction of over 66 percent. Decrease in chemical consumption and a corresponding decrease in the amount of sludge generated led to significant cost savings in the operation of the newly installed co-precipitation unit. In relation to the effluent quality from the co-precipitation system, all permit requirements were met consistently for the treated effluent (TSS<1 mg/L for the co-precipitation system vs. 30 mg/L previously; permit requirement=25 mg/L). Due to the simplicity in operating and maintaining the co-precipitation unit, the plant manager reported that the time devoted to process control and maintenance had reduced significantly resulting in increased operator utilization. Effluent quality as evident from visual observations and chemical analysis was reported to be much cleaner than previous operations.

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OPTIMIZATION STUDY

After the installation of the co-precipitation process, an optimization study was performed to identify optimum operating conditions for maximizing its effectiveness. During the study, the effectiveness of the system was tested at different chemical dosages and flow

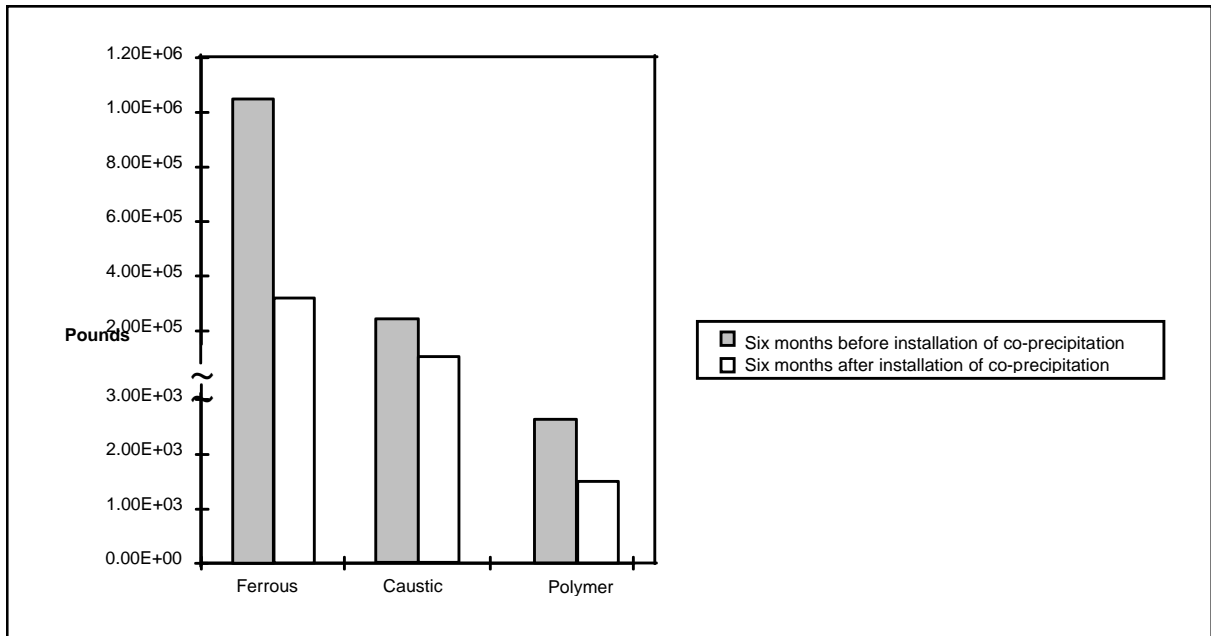


Figure 4. Chemical usage comparison

rates (20, 40, 60 and 70 gpm) to identify conditions that correspond to the best removal efficiency. The influent flow rates were selected to test a representative range within the flow capabilities of the co-precipitation process, from 20 gallons per minute (gpm) to 60 gpm and hydraulic stress at 70 gpm. The dosaging range was chosen to accommodate the varying concentrations of metals observed in the raw water influent during a previous baseline evaluation. The objective in varying the flow and chemical dosages was to

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identify the optimum flow, iron and polymer dosages for operation of the 60 gpm co-precipitation plant.

The effects of several process variables on process efficiency were evaluated to obtain a better understanding of the co-precipitation process and identify optimum parameters or ranges for maximizing system effectiveness. Variables evaluated included: influent water quality, pH range for effective floc formation, flow rates, chemical dosages and solids loading in the reactor. The effects of these variables on process effectiveness are discussed below.

Raw Water Influent Water Quality Variations. During the optimization study, significant fluctuations in the physical characteristics of the wastewater influent were observed. The color of the influent ranged from light green during the first few weeks of the study, to dark brown to black in color and with a sulfur-like odor during the final two weeks of the study. The color of the precipitate in the flocculator varied from brown to gray. In addition, raw water influent TSS, turbidity, and pH varied significantly during the study period. The raw water influent total metals concentrations encountered in this study ranged from 1 to 88 mg/L. The raw water influent TSS ranged from 1 to 118 mg/L, turbidity from 14 to 200 nephelometric turbidity units (NTU), and pH from 8.3 to 12.07.

Effects of Influent Quality.

Variations in the physical and chemical characteristics of the raw water influent had no significant impacts on the metal removal efficiency of the process. However, the effective pH range for coagulation, flocculation and separation of metal precipitates from

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the waste stream shifted significantly with influent water quality variations. To ensure treatment process operation within this effective pH range, pH adjustments were made at the flash mixer to maximize metals removal in the clarifier. The effective pH range for floc formation in this study ranged from 6.35 to 11 and was determined by running simplified screening level jar tests on the raw water. The dark colored influent observed during this study generally had a higher pH range (>10) for effective floc formation. Although the raw water quality and the effective pH for metal removal varied significantly during this study, process parameters were adjusted to cause little to no impact on the process efficiency. The flexibility of the process in accommodating large water quality fluctuations indicate it can be designed to treat a wide range of industrial waste waters. For example, at an influent pH of 10.06, turbidity 200 NTU, total metals 78.5 mg/L, and TSS 118 mg/L, the metal removal efficiency was about 99.1 percent. At a similar pH (10.09), but much lower turbidity of 15.5 NTU, total metals 6.83 mg/L, and TSS 2.5 mg/L, metal removal efficiency was 94.1 percent, indicating that the raw water influent quality parameters such as total metal concentrations, turbidity and TSS did not impact process efficiency.

Flow Rate Variance. Flow rate through the system had minimal effects on treatment since influent flow variations did not impact effluent water quality. For example, in a control test all parameters were kept constant and only the flow rates were varied. Results indicated that flow was not a significant factor in the operation of the co-precipitation system since little to no impacts were observed on the process efficiency.

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Polymer and Iron Dose. Raw water influent metal concentrations encountered in this study were much lower than those encountered during the baseline study. Therefore, iron loading rates of 50 mg/L and higher were used prior to this study to be consistent with the manufacturer's recommended design dosage. The ferrous chloride dosing solution strength (11 percent by volume) and the dosaging pumps were designed for the baseline study influent conditions. However, the raw water influent metal concentrations encountered during this study were much lower than baseline study conditions. Therefore, it was not surprising to see best results at an iron to polymer ratio of 1 to 1 and an iron loading rate in the range of 10 to 25 mg/L. Metal removal efficiency was as high as 99.41 percent for an approximate iron dosage of 10 parts per million (ppm), iron polymer ratio of 1:1 and 60 ppm flow. The iron to polymer ratio was based on the volume flow rate of iron (11 percent by volume ferrous chloride) and polymer (50 percent by volume). While attempting to accurately deliver a lower dosage (10 mg/L) which is one-fifth the design strength (50 mg/L and higher), tuning problems were encountered, and therefore it was difficult to calibrate the pumps to deliver dosages accurately. A lower percentage of ferrous chloride could be used to address this problem.

Solids Loading in the Reactor. Solids loading of about 50 percent in the reactor resulted in good metals removal efficiency. Solids loading less than 10 percent resulted in poor effluent, whereas solids loading greater than 70 percent burdened the clarifier unit. To maintain the desired solids loading in the reactor for nucleation of metal precipitation, the co-precipitation system timers were adjusted to recycle a portion of the

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sludge produced from the clarifier back to the reactor tank while the remaining portion of sludge was pumped to the sludge dewatering facility.

RESULTS AND DISCUSSION

A flow control study was performed with three different step flows (20, 40, and 60 gpm) to identify the optimum flow for operation of the 60 gpm co-precipitation unit process. Although lower flows are known to generally result in substantially higher metal removal efficiencies in water treatment processes that involve clarification (due to increased residence time in the clarifier), in this study, lower flows did not yield significantly higher efficiencies. That is because the lamella-type clarifier of the co-precipitation system evenly distributes the wastewater over a large surface area, minimizing depth of flow, thereby requiring minimal residence time in the clarifier unit for flocculant to settle out. Decrease in the flow rate from 60 (design flow rate for the system) to 20 gpm caused only a 10 percent increase in efficiency.

An iron control study was also performed to compare metal removal effectiveness at three different step flows (20, 40, and 60 gpm) and determine the role of iron in the treatment process. Ferrous chloride was not added in this study, only polymer. The importance of adding ferrous chloride in addition to the polymer was confirmed when the treatment efficiency dropped to 50 percent or less, in the absence of iron dosage.

The system was tested at 70 gpm (hydraulic stress) to determine the effectiveness of the system at its maximum hydraulic capacity. The high metal removal efficiencies obtained for this study (>90 percent for higher polymer:iron dosages) indicate that the system

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could be run at its full capacity, if needed, during peak conditions. Metal removal efficiencies in this test were higher than those encountered for 20 to 60 gpm flows. It is important to note that this 70 gpm study had higher influent TSS concentrations than those encountered in the flow control studies. Higher TSS concentrations could result in heavier floc since the solids aid the agglomeration of particles and subsequent clarification.

Higher iron dosages (> 10 ppm) did not significantly increase treatment effectiveness, but actually decreased in several runs. In a few instances, only a slight increase in efficiency was observed for a five-fold increase (10 to 50 ppm) in ferrous chloride dosages. These observations indicate that a dosage in the range of 10 to 25 ppm ferrous chloride may be in the threshold of diminishing returns. The influent metals concentrations (excluding iron) encountered in this study ranged from 1 to 88 mg/L. However, in the event of a peak or an increase in the influent metal concentrations in future plant operations outside the ranges encountered in this study higher iron and polymer dosages may be required for effective treatment.

Changes in influent metal concentrations could also cause a significant shift in the effective pH range for metal removal. In one instance, a simple jar test was performed in the laboratory when no floc formation occurred at the typical treatment pH of 8.7. The influent was gray to black in color in this instance, which was different from the green to brown color previously observed. During the jar test, good floc formation was observed at pH 10.2, which is outside the co-precipitation recommendation range of 7.5 to 8.5.

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This test indicated that changes in water quality could shift the pH range for floc formation and effective treatment.

RECOMMENDATIONS

Operation of Co-precipitation System. The following recommendations apply to the operation of the 60 gpm co-precipitation system:

- Run system at 10 ppm iron loading, 60 gpm flow (design flow) and an iron polymer ratio of 1:1 to achieve greater metals reduction and reduced sludge generation.
- Particle growth and agglomeration is critical for clarification. Maintain a solids loading of 50 percent in reactor. Lower solids content may result in poor effluent quality. Higher solids content may burden the reactor.
- A reduced ferrous chloride solution concentration source would increase the tuning ability of the existing iron dosing pump. Reduce the ferrous chloride solution strength to 5 percent.
- Adjust the wasting timer to compensate for a smaller amount of sludge produced due to the decrease in chemical dosaging (especially ferrous chloride). Sludge wasting can be conducted less frequently since the lower iron and polymer dosages recommended in this study will result in the generation of lower sludge volumes. Similarly adjust air flow to the reactor and sludge recycling frequency to account for the lower recommended chemical dosaging.

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- Floc formation is critical to effluent water quality; therefore, simple jar tests should be performed to determine the optimum pH for floc formation as changes in influent water quality are observed. Since influent quality can change periodically, visual observations every two hours would help identify water quality variations that could cause a shift in the effective pH range.

References:

1. Unipure Environmental. Dr. Terry Yu, Project Manager.