TRACE HEAVY METALS REMOVAL WITH FERRIC CHLORIDE

Jurek Patoczka, HMM*
Russell K. Johnson, HMM*
John J. Scheri, HMM*

***Hatch Mott MacDonald, Infrastructure & Environment**
27 Bleeker St., Millburn, NJ 07041

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ABSTRACT

This paper presents the results of ferric chloride application in the removal of trace amounts of lead, cadmium, nickel, chromium and zinc, from three different industrial wastewater streams.

For wastewater from a metal picking facility, tests demonstrated that target chromium and nickel concentrations of 0.10 and 0.08 mg/l respectively, could not be achieved by lime precipitation or ion exchange. However, polishing of the lime precipitation supernatant with ferric chloride at a 30-mg/l dose, removed both Ni and Cr to a 0.01mg/l range in unfiltered samples.

The second study involved cadmium, copper, lead and zinc removal from high COD and PHC wastewater found at bus garage floor scrubbing and engine steam cleaning operations. Oil separation with the aid of emulsion-breaking polymers and precipitation using lime or, alternatively ultrafiltration, followed by biological treatment or activated carbon addition, failed to achieve target concentrations of Cd (0.04 mg/l) and Cu (0.75 mg/l). The only method capable of removing critical heavy metals from this complex matrix (stabilized by a high surfactant concentration) was co-precipitation with ferric chloride.

The final application reported in the paper involved lead removal from stormwater, which was generated at a battery-manufacturing site. Chemical precipitation and pH adjustment with the use of different combinations of lime, sodium hydroxide, sodium bicarbonate and trisodium phosphate, did not provide a consistent Pb removal to the target of 0.10-mg/l. Co-precipitation with ferric chloride at a 50-mg/l dose, consistently met treatment objectives at half the cost of an independently proposed, proprietary chemical.

In summary, ferric salts proved to be the method of choice, if not the only feasible method, for removing a variety of heavy metals to sub-mg/l concentration levels from complex industrial wastewater. Due to several different removal mechanisms, ferric salts are capable of removing heavy metals present in soluble, complexed, chelated, colloidal, emulsified and particulate form. This method is particularly applicable for treatment of low-volume industrial steams, where disposal of relatively large quantities of sludge generated, is still an economically competitive solution when compared to other

treatment options; in particular hauling for off-site disposal of the whole wastewater stream.

KEYWORDS

Ferric chloride, ferric hydroxide, lead, nickel, cadmium, copper, chromium

INTRODUCTION

This paper presents three case studies where co-precipitation with ferrous salts was successful in reducing trace concentrations of heavy metals from industrial waste streams to ppb levels, a treatment objective, which was unattainable with more conventional precipitants. Due to a resource limitation on these industrial projects, the scope of experimental and analytical work was restricted to resolving the immediate problem at hand. Consequently, some of the data are fragmentary and without full deployment of the research apparatus, control samples and analytical work, which are necessary for more in-depth evaluation of the underlying mechanisms, wastewater characterization and alternative evaluation. The data present however, a consistent record of ferric salts effectiveness in removal of a variety of heavy metals to low ppb concentration range.

LITERATURE REVIEW

Ferric salts have been recognized as an effective scavenger of heavy metals for a long time and in the literature, extensive treatment has been given to the application and underlying removal mechanism. It has also been recognized that, metals, primarily ferric, hydroxide and oxide coating in the soil and sediments, play an important role in the transport, biotransformation and ultimate fate of trace constituents in natural systems (Benjamin, 1983).

At neutral to alkaline pH, ferric salts precipitate as amorphous hydrated oxide or oxy-hydroxide, which has relatively stable and reproducible surface properties. Upon aging, the precipitate transforms gradually into a crystalline iron oxide (goethite) form. However, its absorptive properties remain quite similar (Murphy et al., 1976, Voges and Benjamin, 1996).

The ability of the ferric hydroxide precipitate to absorb ions with heavy metals is characterized in single and multi-adsorbate systems. Heavy metals could be absorbed both as cations ($Cr+^{3}$, $Pb+$, $Cu+^{2}$, $Zn+^{2}$, $Ni+^{2}$, $Cd+^{2}$) in neutral to high pH, and as anions (SeO_4^{-2}, CrO_4^{-2}, $VO_3(OH)^{-2}$, AsO_4^{-3}) in neutral to mildly acidic pH. A summary of the impact of pH on absorption efficiency for a number of ions can be found in a paper by Manzione et al., (1994). For heavy metals present in cationic form, the absorption efficiency increases with pH, while concentration of both sorbate and ferric hydroxide play a secondary role (Farley et al., 1985). Table 1 provides an overview of the pH needed for 90% removal of selected heavy metals by previously precipitated hydroxide, at different initial heavy metal concentrations in a single-adsorbate system.

Table 1: Minimum pH needed for 90% Removal of Heavy Metals by 60mg/l of Pre-precipitated Ferric Hydroxide (as Fe).

	Pb	Cu	Cd	Zn
Initial Metal Concentration I, mg/l	0.1	0.03	0.06	0.03
Minimum pH for 90% Removal	4.7	5.6	7.2	6.8
Initial Metal Concentration II, mg/l	10	3	6	3
Minimum pH for 90% Removal	5.7	6.4	7.6	7.1

Source: Farley et al., 1985

The mechanism of heavy metals adsorption by the previously precipitated ferric hydroxide, apparently involves different related mechanisms. The adsorption is to a large degree reversible and has been described by both Langmuir and Freudlich adsorption isotherms indicating monolayer coverage (Namasivayam, 1995). A surface complexation mechanism by coordinational bonds, similar to the formation of soluble complexes between solutes and functional groups, has been proposed (Farley et al., 1985, Benjamin, 1982). Due to displacement of the hydrogen ion from the surface during the adsorption, elements of an ion-specific ion exchange adsorption have been postulated (Gadde and Laitnen, 1974). A unifying model, apparently capable of describing data from a wide range of experimental conditions of pH and concentration, has been proposed by Farley et al. (1985). It provides a continuum between monolayer coverage at a lower concentration and transition to surface precipitation at higher concentrations.

In practical applications, ferric hydroxide is precipitated in situ, which facilitates incorporation of heavy metal cations directly into the precipitate matrix in place of the similarly sized and charged ferric cations; mechanisms known as co-precipitation. This would account for only partial reversibility of the metal adsorption reaction upon reversal of pH.

It has been a common experience (including data in this study) that pH-induced precipitation based on theoretical hydroxide (or hydrated oxide) solubility, frequently fails expectation. One of the likely reasons for higher than expected concentration of metals in soluble form, is the formation of chelates or complexes. The list of potential complexing agents is extensive and may include for various heavy metals, such diversified and ubiquitous substances as ammonia, chlorides, sulfates, cyanides, amines, thiourea, citric acid, and other organics. This includes agents specifically used in industrial applications for their chelating properties, such as EDTA (Choo, 1992). Ferric salts appear to be capable of overcoming the masking effect of complexing agents or chelating ligands, perhaps by replacing trace heavy metal by the ferric cation.

An additional problem, which limits effectiveness of pH-induced precipitation of heavy metals, is the presence of emulsions and colloids stabilized by surfactants commonly found in industrial wastewater. Metals could be encapsulated into colloidal particles or emulsion globules (including in dissolved form), where they are relatively resistant to pH changes in the bulk liquid. Since ferric salts are also coagulants, their practical effectiveness in heavy metal removal extends into colloidal, emulsified and fine particulate forms of heavy metals.

It should be mentioned that ferric salts are themselves ubiquitous in waste streams where other heavy metals are present, and are likely responsible for better than theoretically expected removal of heavy metals from some streams, by pH induced precipitation (Boiling, 1991).

Many alternative chemicals/processes were proposed/used for heavy metal removal. Some of the examples are organic precipitants such as DTC, (alkyl dithiocarbamates) which is used in the treatment of printed wiring boards, wastewater, (Choo, 1992), modified natural zeolites (Groffman, 1992) and membrane filtration (micro-, ultra- and nano-filtration) (Capaccio, 1996). Their application in many practical situations is however limited, due to various interferences, development and control costs, maintenance problems and process limitations.

Case Study 1: Removal of Cr and Ni from Metal Pickling Wastewater

A small stainless steel tubing manufacturer was generating approximately 7.5m^3 (2,000 gallons) of wastewater every two weeks from a pickling process, which utilized a 15% nitric acid and 2.5% hydrofluoric acid pickling bath. The wastewater originated from rinse tank overflow and fresh water wash, with typical composition given in Table 2. The contaminants of interest in this study were chromium and nickel present in the raw wastewater at high concentration, due to the nature of the raw material (stainless steel). Pretreated wastewater was discharged to sewers for treatment at a local municipal biological treatment plant.

Table 2: Case Study 1 - Typical Composition of Wastewater and Treatment Objectives.

Parameter, mg/l (except pH)	Raw Water	Lime Treated Wastewater	Existing Source Categorical Limits (1)	New Source Categorical Limits (1)
Cr (total)	40 – 110	0.2 – 0.6	1.1	0.10
Cr (+VI)	<1.0	0.05 – 0.60		
Ni	30 – 100	0.1 – 0.2	0.83	0.08
Fe	500 – 800			
COD	60			
TDS	1,500 – 2,300			
pH	1.5 – 2.0			

(1) Estimates of monthly average limits based on the expected production rates and wastewater generation.

Originally, pretreatment consisted of batch neutralization with sodium bicarbonate, which removed the majority of chromium, nickel and ferric to a residual concentration of several mg/l range. In 1991, the pretreatment was upgraded to include lime precipitation with subsequent neutralization, in order to meet Categorical Pretreatment Standards for existing Sources (Table 2). As indicated in Table 2, lime treatment was adequate to meet the Existing Source limits of 1.1mg/l and 0.83mg/l for Cr and Ni, respectively.

Due to the relocation of the manufacturing facility, it was determined that the discharge would have to meet more stringent Pretreatment Standards for New Sources. As it is apparent from Table 2, the existing lime-based pretreatment was not capable of consistent removal of Cr and Ni to the new sub-mg/l limits.

One of the polishing methods initially considered for this application, was ion exchange. Thus, a sample of lime-treated wastewater was submitted for testing to a major ion exchange manufacturer. The laboratory concluded that the discharge limit of 0.10mg/l for Cr was not attainable using ion exchange, due to the presence of competing ions (640mg/l of Ca^{+2} from lime treatment) and technology (ion exchange) limitations. The Resin manufacturer's past tests with various Cr^{+3} solutions indicated that, ion exchange can remove this cation to no less than 0.25mg/l. Consequently, this alternative was eliminated from further evaluation, leaving precipitation with different agents as the most viable alternative.

Due to the adequate performance of the lime precipitation, it was previously presumed that Cr is present in the trivalent form. With the new more stringent limits, presence of traces of hexavalent Cr if any, became important as Cr^{+6} is soluble in neutral to high pH range. Since high concentrations of Cr^{+3} present in the raw wastewater interfered with colorimetric determination of the Cr^{+6} at the ppb level of interest in this study, determinations of the residual Cr^{+6} were conduced on a sample treated with lime, for the removal of the bulk of Cr^{+3} (and Ni). Testing of several lime-treated effluent samples, indicated the presence of Cr^{+6} in the 0.05 to 0.6mg/l range indicating that, reduction of residual Cr^{+6} was necessary to meet new sub-mg/l limits by precipitation.

The initial reduction tests were performed with the use of sodium bisulfite ($NaHSO_3$) and ferrous sulfate ($FeSO_4$) at doses of 2 and 10mg/l, which were in excess of the stoichiometric requirement. A reaction contact time of 10 to 15 minutes was used, which was reported (Beevers, 1972) to be adequate to bring the reduction reaction to practical completion at the pH range of 1.5 to 2 SU experienced in the raw wastewater. Subsequently, heavy metals were precipitated with lime at a range of pH and then settled overnight with an aid of 15mg/l of an ionic polymer. From the results of these limited tests performed on a single wastewater sample, (Table 3) the following conclusions were apparent:

- No reduction of the Cr^{+6} was accomplished by the use of the two individual reducing agents, although the initial Cr^{+6} concentration was very low 950ppb).
- Lime treatment at pH of 10.5 SU or higher, removed Ni to adequate levels (in unfiltered samples).
- Even without Cr^{+6} present, lime treatment alone did not offer a consistent performance for Cr removal.

The effectiveness of the reduction reaction was tested again on wastewater samples from two different batches using the same individual reducing agents, but at higher concentrations of 20 and 100mg/l in separate tests. The results again demonstrated a lack of adequate reduction with the use of the ferrous sulfate and sodium bisulfate alone under the conditions.

One other widely used hexavalent chromium reducing agent, hydrazine, was not tested due to safety concerns on the part of the user.

Based on a literature lead (Voges and Benjamin, 1996), it was decided to use a combination of the two previously used reducing agents at an even higher dose of 200mg/l each. Due to the very low Cr^{+6} concentration in the available sample, the sample was first spiked with 0.20mg/l of Cr^{+6} in a form of potassium dichromate. Following the reduction reaction and standard lime treatment, the supernatant samples were tested with the results shown in Table 4. At this time, it was also decided to evaluate the effectiveness of co-precipitation with ferric hydroxide for removal of the residual Cr and Ni, following reduction and lime treatment. For that purpose, ferric chloride at a 30mg/l dose was added, pH adjusted to approximately 8 SU and wastewater settled following 30 minutes flocculation time. Additionally, control samples with lime treatment only, as well as with lime and ferric chloride only, were run in parallel. As the data presented in Table 4 indicates, the treatment proved to be successful in terms of both reduction of Cr^{+6} and metal (Cr and Ni) removal.

Table 3: Case Study 1 - Reduction of Cr (VI) by Ferrous Sulfate and Sodium Bisulfite Followed by Lime Precipitation in Sample #1.

Treatment: Reducing chemical dose, final pH after lime treatment	Total Ni	Diss. Ni	Total Cr (III + VI)	Total Cr (VI)	Diss. Cr (III + VI)
2mg/l FeSO4 pH = 9.45	0.110	0.023	0.181	0.050	0.063
pH = 10.47	0.030	0.006	0.153	0.070	0.094
pH = 11.01	0.064	0.005	0.207	0.080	0.091
10mg/l FeSO4 pH = 9.58	0.071	0.019	0.130	0.040	0.156
pH = 10.20	0.056	0.006	0.126	0.040	0.051

pH = 11.12	0.044	<0.005	0.142	0.060	0.075
2mg/l NaHSO3 pH = 9.62	0.056	0.020	0.099	0.040	0.058
pH = 10.35	0.034	<0.005	0.108	0.050	0.053
pH = 11.27	0.036	<0.005	0.153	0.0060	0.070
10mg/l NaHSO3 pH = 9.48	0.067	0.022	0.112	0.050	0.061
pH = 10.50	0.037	0.005	0.134	0.060	0.067
pH = 11.18	0.034	<0.005	0.129	0.060	0.062

Table 4: Case Study 1 - Cr (VI) Reduction and Cr and Ni Removal by Sequential Treatment with Lime and Ferric Chloride in Sample #2.

Treatment	Total Ni	Diss. Ni	Tot. Cr (III + VI)	Tot. Cr (VI)	Diss. Cr (III + VI)
Raw Wastewater (pH 1.5)	64.7	64.3	101	<1.0	101
Lime only (pH 10.5)	0.323	0.019	0.673	0.073	0.117
Reducing agents plus lime (pH 10.5)	0.126	0.008	0.209	0.009	0.027
Lime (pH 10.5) plus ferric chloride (pH 8)	0.010	0.007	0.062	0.049	0.037
Reducing agents (pH 1.5) + lime (pH 10.5) + ferric chloride (pH 8)	0.011	0.006	0.009	0.001	0.005

Following successful jar tests, the treatment system was modified to accommodate sequential reduction/lime/ferric chloride treatment in a batch-wise mode in a 7.5m^3 (2,000gallons) tank. The procedure has been successfully utilized in full scale on more than a dozen batches of wastewater without a single problem. The highest chromium and nickel concentrations recorded in the effluent were 0.035 and 0.06mg/l respectively, well within the permit limit. The sludge generated in the process is collected in a separate tank, decanted and disposed of off-site. It should also be noted that, it was recognized that wastewater treated with ferrous sulfate contained sufficient quantities of iron to generate adequate amounts of ferric hydroxide upon aeration, without addition of the ferric from an outside source. In this particular situation however, it was more practical to add minuscule amounts of chemical, (0.5 liters of 30% $FeCl_3$ solution per batch) than to experimentally document the aeration option and install the necessary aeration equipment.

Case Study 2: Lead Removal from Stormwater on Battery-Manufacturing Site

This project involved the development of a treatment scheme for lead-contaminated stormwater from a large site of a battery manufacturer. The runoff from roofs, parking lots, driveways and ground, was to be contained in a storage tank from which it was to be pumped and treated, prior to direct discharge to a stream. The critical contaminant of concern was lead, with a NPDES limit of 0.19mg/l as a monthly average. The treatment plant flows considered for the design were from 380 to 1,140m^3/day (100,000 to 300,000gpd), depending on the selected size of the storage tank.

As expected, Pb concentrations in the site runoff varied as a storm progressed, with an average value of about 0.5 to 2mg/l. Most of the load was in a soluble form (as filtered through Whatman 934-AH paper). In some first flush samples, much higher concentrations were reported, primarily in suspended form.

In order to consistently meet 0.19mg/l as monthly average permit limit, 0.10mg/l was selected as the design effluent concentration and target concentration for the treatability study. From the information on the Pb concentration profile, it was apparent that no opportunity for stream segregation existed and all stormwater would have to be treated.

Initially, the treatability work concentrated on pH adjustment/chemical precipitation. It was also recognized that some kind of filtration step would be most likely necessary in full scale. Thus, analytical samples from treatability work were filtered through a Whatman 934-AH membrane.

The initial list of treatment included various combinations of lime (CaO), caustic (NaOH) and sodium carbonate (Na_2Co_3). The typical jar test procedure included, pH adjustment with lime or caustic to a target value in the 7 to 10.5 SU range, 5 to 10 minute flocculation and 30 minute settling. To facilitate pH adjustments, titration curves for lime and caustic were first developed. Additional tests with sodium carbonate with and without subsequent pH adjustment were performed, following literature information that such supplementation of alkalinity was effective for lead hydroxide precipitation (Paterson, 1985).

The results are presented in Figure 1 and clearly indicate that conventional pH adjustment/precipitation was not effective for bringing Pb to the target concentration of 0.10mg/l.

Subsequent tests included evaluation of three additional chemicals: ferric chloride ($FeCI_3$), trisodium phosphate (Na_3PO_4) and PQA, a proprietary agent reported to be successful in trace lead removal at another site owned by the user. Side by side tests with use of these chemicals were conducted on three different wastewater samples at the target pH of 8 SU. This was the pH recommended by the developer of PQA as optimal. At the same time literature sources (Table 1) indicated that, ferric hydroxide should be effective for lead adsorption at pH higher than 6.0. This was confirmed by some additional tests with $FeCI_3$ conducted at a range of pH. Trisodium phosphate was not effective at doses up to 100mg/l in the first round and so, it was no longer considered. Jar test procedures were as detailed above, with the summary of the results for $FeCI_3$ and PQA presented on Figures 2 and 3, respectively, for 3 different wastewater samples. (Note that the initial lead concentration for some samples was different for different chemicals, due to the fact that some tests were not conducted at the same time).

Figure 1

Pb Precipitation by pH Control

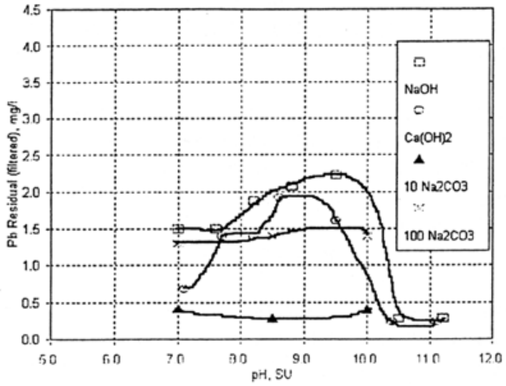


Figure 2

Summary of FeCl3 results @pH8

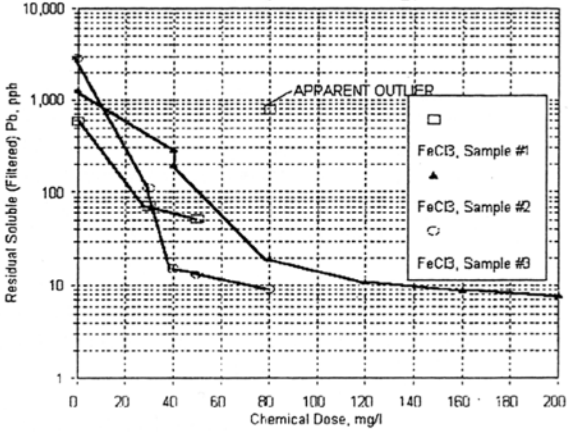


Figure 3

Summary of Results with PQA @ pH8

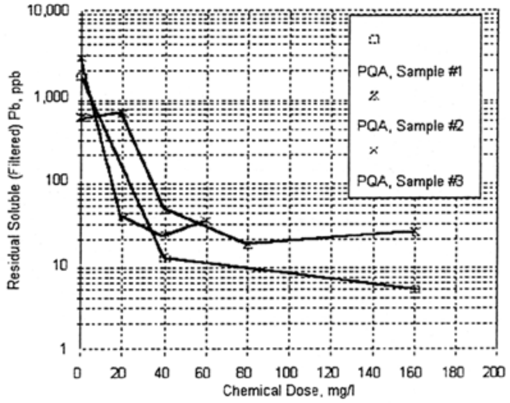
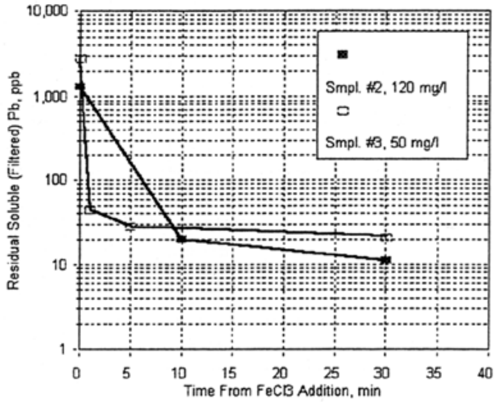


Figure 4

Reaction Time Test with FeCl3 @pH 8



Based on Figures 2 and 3, the effective doses to meet the target 0.10mg/l ppb level in all samples tested, were 50 and 30mg/l for $FeCI_3$ and PQA respectively. However, due to much higher unit cost of the proprietary PQA, ferric chloride was recommended by more than a 2:1 ratio, as the more economical alternative. The required dose of ferric chloride was much higher than recommended by Macchi (1993) in his lead battery wastewater application, where ferric dose was based on Fe/Pb ratio.

The flocculating time required for the completion of the co-precipitation/adsorption was evaluated in separate jar tests. They demonstrated that after 10 minutes, the reaction was practically completed from the standpoint of this particular application (Figure 4). This flocculation time was used in the jar tests and subsequently recommended as a minimum contact time for design. The recommended treatment scheme also included the addition of anionic polymer at 0.5mg/l dose, which was found in jar tests to be an effective settling aid.

Case Study 3: Cadmium, Copper, Lead and Zinc Removal from High COD and PHC Wastewater from Bus Garage

This study involved cadmium, copper, lead and zinc removal from high COD and PHC wastewater, found at bus garage floor scrubbing and engine steam cleaning operations. The average rate of the heavily contaminated wastewater evaluated in this study was 5.7m^3/d (1,500gpd). The existing pretreatment system, which also treated 17m^3/d (4,500gpd) of lightly contaminated bus washing wastewater, included a sand/grit interceptor and oil-water separator. The effluent, which was discharged to a municipal agency collection system, failed to meet final pretreatment standards of BOD_5, TSS, COD, O&G, PHC and heavy metals (Cd, Cu, Pb and Zn), most of the time.

Stream characterization indicated that, bus wash wastewater could be discharged directly without pretreatment, facilitating segregation and treatment of the heavily contaminated streams. The expected typical composition of the segregated wastewater (excluding bus wash wastewater) is shown in Table 5.

Table 5: Case Study 3 - Typical Composition of Bus Garage Wastewater

Parameter	Typical concentration, mg/l (except pH)	Final Pretreatment Limit
BOD_5	2,000	500
COD	5,200	750
Oil & Grease	2,400	75
PHC	1,250	10
TSS	4,000	500
pH	10 – 11	6 – 9
Cadmium	0.30	0.04
Copper	3.7	0.75
Lead	2.4	0.3
Zinc	8.5	3.0

The initial treatment methods screened included:

- Settling and oil/water separation with aid of several emulsion-breaking polymers and alum in various combinations.
- Ultrafiltration.

Effluents from the above listed treatments were then subjected to polishing by activated sludge in batch tests or by activated carbon adsorption. Procedural details and results of the various treatment combinations used are beyond the scope of this paper, and only a summary review of the results is provided, followed by more detailed information on heavy metals removal.

In general, chemical treatment with emulsion breaking polymers and alum in various combinations and doses, demonstrated limited ability to adequately remove organic matter (COD an d PHC). The wastewater pretreated with a selected emulsion breaker at a 200mg/l dose achieved the target COD and PHC, only after polishing by activated sludge in a batch test.

Similarly, ultrafiltration tests conducted by a membrane manufacturer on two different membranes failed to achieve target COD and O&G levels. Permeate had to be subsequently polished by activated sludge for adequate removal of these constituents.

The critical problem however, was posed by heavy metals. None of the treatment combinations tested so far was capable of adequate removal of heavy metals, in particular Cd and Pb. Consequently, subsequent tests included pH adjustment and chemical precipitation with lime and ferric chloride.

Initially, a series of simple pH adjustments/precipitation tests were performed in the range of 8.7 to 11.1, with NaOH and lime. Following adjustment to the desired pH, the sample was flocculated for 30 minutes, settled and supernatant analyzed for dissolved (filtered through Whatman 934-AH filter) metals. The results were quite disappointing (Table 6), as high residual heavy metals concentrations were present in all samples, regardless of the pH. It is likely that heavy metals were complexed by constituents of industrial cleaners and other chemicals present in the wastewater.

Table 6: Case Study 3 - Results of Heavy Metal Removal with NaOH and Lime – Sample #3

Treatment	Cd, mg/l	Cu, mg/l	Pb, mg/l	Zn, mg/l
Original Sample, pH = 8.7	0.17	0.57	0.93	2.4
Permit Limit	0.04	0.75	0.30	3.0
NaOH Adjusted to pH 9.8	0.13	0.48	0.70	1.8
NaOH Adjusted to pH 10.1	0.15	0.56	0.77	2.0
NaOH Adjusted to pH 11.1	0.15	0.63	0.68	1.5
Lime Adjusted to pH 10.6	0.15	0.56	0.69	1.4

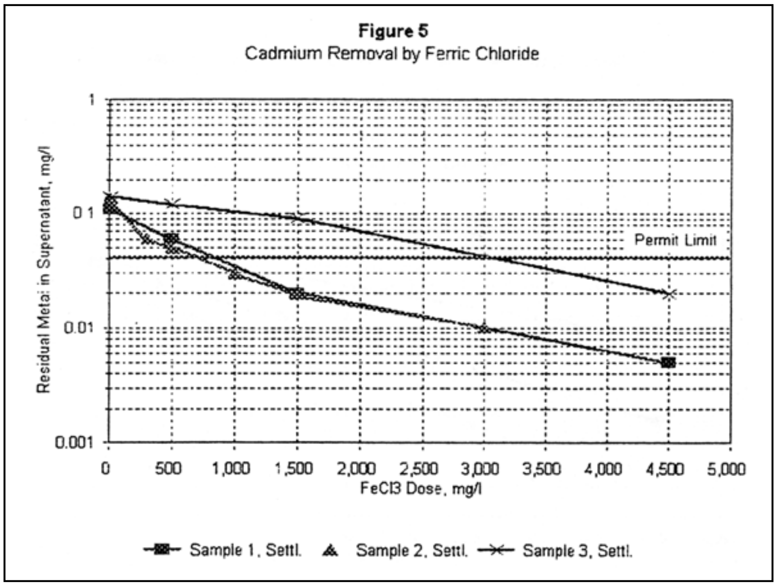


Figure 5
Cadmium Removal by Ferric Chloride

As in the previous projects, the chemical of last resort, which was ferric chloride, was used. Following ferric chloride addition, the pH was adjusted to 7.5 (in accordance with information in Table 1), sample flocculated for 30 minutes, settled and heavy metals analyzed, in filtered and unfiltered supernatants.

The treatment was successful, as high enough doses were capable of removing all the metals to below detection limits even in settled only samples. The tests were repeated on a total of 3 different samples of the wastewater, and are summarized for the individual metals (settled samples) in Figures 5 through 8. The most difficult to remove were Cd and Pb, requiring doses in excess of 3,000mg/l not entirely surprising, considering the complexity of the matrix and high background organics concentration.

Figure 6
Copper Removal by Ferric Chloride

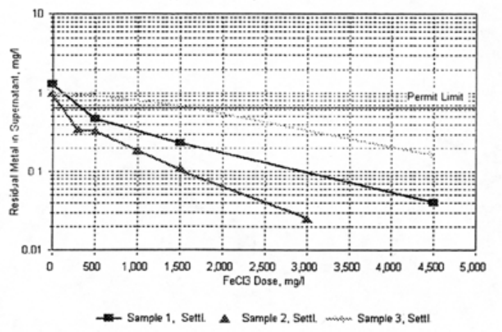


Figure 7
Lead Removal by Ferric Chloride

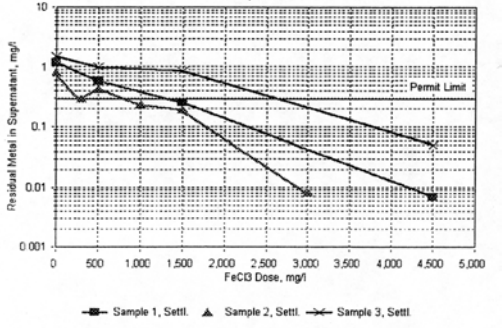
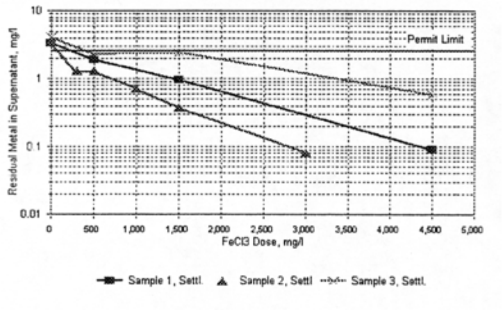


Figure 8
Zinc Removal by Ferric Chloride



In summary, the only identified and verified method for removal of heavy metals and organics to the required level was co-precipitation/adsorption with ferric chloride, followed by polishing, by activated sludge or activated carbon for organics removal.

The obvious problem created by use of 3,000mg/l ferric chloride dose was the large volume of generated sludge, which constituted between 10 to 15% of the wastewater volume (upon 30 minute gravity settling, without thickening/pressing). However, the only other viable alternative was hauling of the entire 5.77m³ (1,500gpd) of heavily contaminated stream for outside disposal.

Present worth analysis indicated that costs of the onsite treatment, including sludge processing and disposal over the life of the project, were somewhat higher than off-site disposal of the entire 5.7m³ (1,500gpd) of the heavily contaminated streams, under then prevailing off-site disposal costs. It is expected however that, in the future, construction of a pretreatment facility might become a necessity due to increasing off-site disposal costs and potentially more stringent pretreatment limits (necessitating treatment of the presently discharged lightly contaminated waste stream).

SUMMARY

Three different industrial wastewater streams contaminated with various heavy metals (lead, cadmium, nickel, chromium, copper and zinc) were evaluated for identification of practical treatment technology. The conventional precipitation induced by pH control, failed to achieve the required goals at sub-mg/l levels for chromium, lead, cadmium and nickel. In each case, adsorption/co-precipitation with ferric chloride proved to be effective. This method is particularly applicable for treatment of low-volume industrial streams, where disposal of relatively large quantities of sludge generated, is still an economically competitive solution when compared to other treatment options; in particular hauling for off-site disposal of the entire wastewater stream. In such small-scale applications, development and implementation of other treatment alternatives generating potentially lower amounts of residuals, is frequently not justified due to cost. Treatment with ferric salts offers a robust option, capable of removing heavy metals to ppb levels from complex matrix with metals present in various forms such as dissolved, colloidal, emulsified and particulate.

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