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Project Summary

Alternative Processes for Treatment of Sinter Plant Wastewater

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With the promulgation of Best Available Technology Economically Achievable (BAT) Effluent Guidelines and Standards for Iron and Steel Manufacturing, a greater degree of treatment than the clarification process normally used to achieve best practicable technology (BPT) standards may be required for sintering plant blowdown. This study evaluated the effectiveness of two treatment alternatives in achieving the BAT standards: (1) direct filtration, using a dual media filter; and (2) hydroxide precipitation with lime, followed by dual media filtration. Evaluation of a third alternative, alkaline chlorination, was attempted; but, due to nonrepresentative test conditions, the effort was abandoned.

The treatment processes were tested, using two EPA-owned mobile pilot plant trailers: one contained a clarifier, used to simulate preclarification; and the other contained the hydroxide precipitation clarifier, chemical tanks, dual media filter, and associated equipment.

The limited data generated during the study indicate that either treatment alternative tested would produce an effluent that would meet the promulgated BAT standards. Direct filtration is less expensive and requires less maintenance and operator attention than the hydroxide precipitation/filtration alternative.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Under the Effluent Guidelines and Standards for the Iron and Steel Manufacturing Point Source Category promulgated May 27, 1982, Best Available Technology (BAT) effluent limitations for the Sintering subcategory are based on applying a higher degree of treatment than BPT clarification alone. Pilot plant studies were conducted to evaluate two treatment alternatives for removal of selected pollutants for which BAT limitations had been proposed.

> NOTE: This study was conducted before the May 27, 1982, promulgation of the BAT Effluent Limitations for the Iron and Steel Manufacturing Point Source Category. The basis for the selection of pollutant parameters for evaluation of the alternative treatment systems investigated in this study was the proposed guidelines made public in December 1980. This report has been updated to indicate the promulgated guidelines.

The treatment alternatives piloted were: (1) direct filtration, employing a dual media pressure filter; and (2) hydroxide precipitation with lime, followed by dual media filtration. A third alternative, alkaline chlorination, was attempted; but, due to an intermittent production schedule during this test phase, representative samples were not collected. The wastewater tested was blowdown from the venturi scrubber and cyclonic mist eliminator wet air pollution control system. Wastewater analyses quantified suspended solids, fluoride, cyanide, phenols, oil and grease, and various heavy metals and priority pollutants.

The major objective of the testing program was to develop a data base from which the alternative treatment systems could be evaluated both individually and comparatively. The data base was generated through laboratory analyses of regularly collected samples and monitored operating conditions during pilot plant operation. To assess the performance of each process, the data was analyzed for removal of selected pollutants. Capital and operating costs were developed to assess the economics of each process application. An overall comparative evaluation was then made, based on both performance and economics.

Summary

Testing Program Description

Trailer-mounted pilot facilities were used to test two treatment alternatives for sinter plant blowdown: (1) direct filtration, using a dual media filter; and (2) hydroxide precipitation with lime, followed by dual media filtration. The pilot plant consisted of two existing EPA-owned trailers, part of the Mobile Wastewater Treatment System (MWWTS) designed to provide treatment for a nominal throughput of 5 gpm.* Trailer No. 1 contained the chemical treatment system and filtration equipment. Trailer No. 2 contained a clarifier for preclarification, required since the influent to the pilot plant was tapped from the sintering blowdown line prior to treatment with other waste waters in an existing on-site clarifier.

Flow trains for the direct filtration and hydroxide precipitation followed by filtration treatment alternatives are shown in Figure 1. Filtration is common to both alternative BAT treatment models that were tested in the pilot study. Direct filtration of sintering blowdown was evaluated for removal of suspended solids and other pollutants (e.g., metals, which may be in particulate—nonsoluble—form). In the hydroxide precipitation alternative, filtration of clarified effluent is a polishing step for removing the metal hydroxides that are not removed by clarification.

The filter media consisted of 12 in. of sand, with a particle size in the range of 0.4 to 0.8 mm, and 24 in. of anthracite, with a particle size of 1.0 to 1.5 mm. The hydraulic loading rate to the filter was kept at approximately 5 gpm/ft^2 during the tests.

Precipitation of heavy metals as hydroxides through the addition of lime is a well-established technology. Lime is added to raise the pH to a level found to be the most suitable for optimum precipitation of the metal hydroxides which are of concern. The metal hydroxide precipitates form a floc which can entrain particulates, including other metallic forms, and thus enhance their removal. In addition to removing metals, hydroxide precipitation with lime can also remove fluoride by providing a source of calcium for precipitation of calcium fluoride.

Although hydroxide precipitation is relatively simple, it has several limitations. Its effectiveness in removing heavy metals is a function of the solubility of the metal hydroxides which, in turn, is a function of pH and water quality. Thus removal of heavy metals is limited to the solubility of the metal hydroxides in the particular wastewater matrix under consideration. Based on bench scale data and previous experience with hydroxide precipitation of heavy metals, the pilot tests were run at an operating pH of 10. A slurry of hydrated lime—$Ca(OH)_2$—was applied to the wastewater in a rapid mix tank to maintain a pH of 10. The wastewater then flowed by gravity to a flocculator/clarifier for flocculation and settling.

Eight-hour composite samples of raw wastewater (pilot plant influent), clarifier effluent (during the hydroxide precipitation testing phase), and final (filtered) effluent were collected automatically and analyzed for selected pollutant parameters.

The analytical work performed for this study incorporated quality control analyses, including method and reagent blanks, field replicates, laboratory replicates, standards and spikes. The quality control data was monitored daily. All samples received by the laboratory were logged in and processed immediately upon receipt to ensure that holding times were not exceeded.

The selected pollutant parameters for the sinter plant pilot testing included suspended solids, pH, fluoride, cyanide, phenols, oil and grease, and certain heavy metals and priority pollutants. These parameters (shown in Table 1) were used to develop a data base for evaluating the alternative treatment processes.

Plant Site

Pilot testing was conducted at the Armco Steel Corporation, Middletown, Ohio, Works. The sinter plant converts iron-bearing waste fines into blast furnace feed materials. During the pilot plant test period, the feed to the sinter

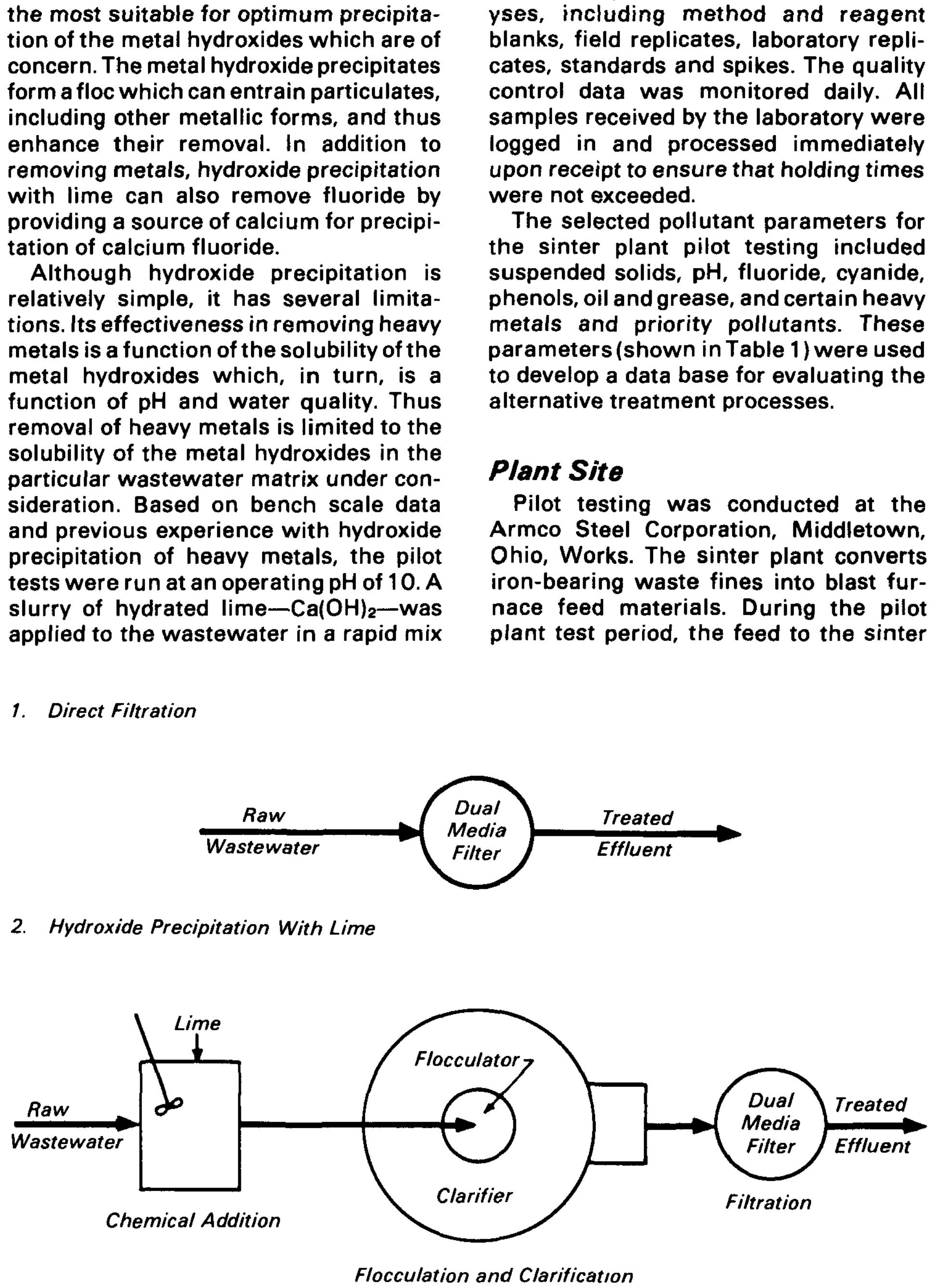

Figure 1. *Pilot plant process flow trains.*

(*) Readers more familiar with metric units may use the conversion factors at the back of this Summary.

Table 1. Pollutant Parameters Selected for Pilot Testing of Sinter Plant Blowdown

Phenols (4 AAP)	*Cadmium*
Fluoride	*Chromium*
Suspended Solids	*Copper*
Oil and Grease	*Cyanide*
pH	*Lead*
Fluoranthene	*Nickel*
Phenol	*Silver*
Chrysene	*Zinc*
Pyrene	

plant consisted of approximately 70 percent BOF slag, 15 percent taconite fines, 12 percent blast furnace scrubber sludge, and 3 percent coke fines.

Waste gases from the sinter plant are cleaned by a venturi scrubber and cyclonic mist eliminator. Blowdown, taken directly from the bottom of the mist eliminator tank at a rate of 325 gpm, comprises about 15 percent of the mist eliminator flow. The balance of the flow is recirculated back to the scrubber.

Results and Evaluation—Summaries of the direct filtration data and hydroxide precipitation/filtration data are given in Tables 2 and 3, respectively. To ensure representative values, unusually high or low values have been dropped from the averages and ranges in these tables. Priority pollutants that were detected are given in Table 4.

The promulgated BAT and BPT limitations are given in Table 5.

The two processes were compared with respect to effectiveness in removal of the selected pollutant parameters. Direct filtration was effective in removing all of the selected pollutant parameters found to be present in the sinter plant blowdown in significant quantities. The degree of chromium and zinc removal varied with varying levels of soluble chromium and zinc in the influent. Cyanide, present in very low levels, was not affected. All of the BAT and BPT Effluent Limitations were met by the direct filtration effluent. Filter operation is simple and easily controlled, requiring minimal operator attention. No sludge is produced. The backwash solids load that is intermittently generated could be recycled to the head of most existing BPT treatment systems without any additional treatment.

Hydroxide precipitation followed by filtration was effective in removing all of the selected pollutant parameters found to be present in significant quantities, except phenols. The degree of chromium removal varied with the level of soluble influent chromium. Cyanide, present in very low levels, was not affected. All of the BAT and BPT Effluent Limitations were met by the hydroxide precipitation and direct filtration effluents. Operation is straightforward and could be automatically controlled with a high level of reliability. Operations manpower would be mainly for lime slurry batching, system monitoring, and routine maintenance. The waste sludge which is produced can be treated and disposed of along with BPT sludge at most plants by employing existing BPT facilities.

Both treatment processes performed well; however, neither performed significantly better than the other. Hydroxide precipitation achieved slightly lower residuals for most parameters than direct filtration. Direct filtration produced a high quality effluent at a significantly lower cost and less operational considerations and, therefore, best achieved the goals of BAT.

Because heavy metals in the sinter plant blowdown were predominantly in particulate form, direct filtration was effective in removing them. If significant quantities of soluble metals had been present, its effectiveness would have been considerably less. Therefore, this evaluation is based on the sinter plant blowdown that was treated during the study.

Economic Analysis

Estimated capital costs and operating costs for the direct filtration and hydroxide precipitation with filtration processes are given in Table 6. Construction costs were developed for treatment facilities de-

Table 2. Direct Filtration Data Summary

Parameter	Preclarifier Influent (ppm)		Number of Samples[a]	Pilot Influent (ppm)		Number of Samples[a]	Filter Effluent		Number of Samples[a]	Average % Removed
	Mean	Range		Mean	Range		Mean	Range		
Suspended Solids	1644	120-5210	5	123	15-210	11	3	1-7	11	98
pH	7.9	7.3-8.6	5	7.8	6.9-9.1	12	7.8	6.9-9.0	12	--
Fluoride	109	15-250	5	18	9-29	12	16	10-34	11	11
Phenol	0.23	0.04-0.60	5	0.10	0.01-0.30	12	0.07	0.01-0.22	12	30
Cyanide	0.07	0.047-0.094	4	0.14	0.075-0.250	12	0.130	0.034-0.26	12	--
Oil & Grease	158	28-310	6	<9	<5-20	6	<6	<5-9	6	--
Total Cadmium	0.017	<0.010-0.034	5	<0.011	<0.010-0.020	12	<0.010	<0.010-0.013	12	--
Total Chromium	0.362	0.110-0.580	5	0.265	0.050-0.500	12	0.170	0.010-0.430	12	36
Total Copper	0.150	0.079-0.220	5	0.038	0.020-0.086	12	<0.020	<0.020-0.026	12	--
Total Lead	0.490	0.290-0.790	5	0.140	0.034-0.340	12	<0.0200	<0.0200	12	>86
Total Nickel	0.140	0.032-0.290	5	<0.021	<0.01-0.042	12	0.013	<0.01-0.023	12	38
Total Silver	0.0130	<0.010-0.025	5	<0.010	<0.010	12	<0.010	<0.010	12	--
Total Zinc	13	6.7-20	5	0.78	0.27-2.6	11	0.18	0.06-0.47	12	77

[a]*Except for the Preclarifier, for which fewer samples were taken, the number of samples may vary due to unusually high or low data values which were dropped from the averages and ranges. Six oil and grease samples were taken at each sampling point.*

Table 3. *Hydroxide Precipitation Data Summary*

Parameter	Preclarifier Influent (ppm) Mean	Range	Number of Samples[a]	Pilot Influent (ppm) Mean	Range	Number of Samples[a]	Clarifier Effluent (ppm) Mean	Range	Number of Samples[a]	Filter Effluent (ppm) Mean	Range	Number of Samples[a]
Suspended Solids	143	34-380	4	42	3-76	11	47	4-92	12	<2	<1-3	10
pH	7.9	7.6-8.1	4	7.8	7.6-8.2	12	9.9	9.6-10.3	12	9 9	9.5-10.3	12
Fluoride	193	20-270	4	23	13-58	12	15	12-22	10	16	11-24	12
Phenol	0.32	0.14-0.40	4	0.12	0.06-0.22	10	0.16	0.10-0.30	11	0.16	0.10-0.30	11
Cyanide	0.03	0.03-0.04	4	0.08	0.05-0.13	11	0.07	0.02-0.11	12	0.07	0.03-0.11	12
Oil & Grease	191	76-270	8	5	4-7	8	3	1-5	8	<2	<1-4	8
Total Cadmium	<0.019	<0.010-0.036	4	<0.010	<0.010	12	<0.010	<0.010	12	<0.010	<0.010	12
Total Chromium	0.209	0.170-0.280	4	0.185	0.075-0.470	12	0.140	0.025-0.290	12	0.132	0.020-0.240	12
Total Copper	0.114	0.072-0.160	4	<0.026	<0.020-0.049	12	<0.020	<0.020	12	<0.020	<0.020	12
Total Lead	0.86	0.27-1 1	4	0 096	<0.02-0.200	12	0.034	<0.020-0.180	12	<0.020	<0.020	12
Total Nickel	0.124	<0.010-0.370	4	0.014	<0.010-0.036	12	0.014	<0.010-0.033	12	<0.010	<0.010	12
Total Silver	<0.022	<0.010-0.057	4	<0.010	<0.010	12	<0.010	<0.010	12	<0.010	<0 010	12
Total Zinc	21	2.8-64	4	0.63	0.13-3.8	12	0.04	0.02-0.08	12	<0.01	<0.01-0.01	12

[a]*Except for the Preclarifier, for which fewer samples were taken, the number of samples may vary due to unusually high or low data values which were dropped from the averages and ranges. Only 8 oil and grease samples were taken at each sampling point.*

Table 4. *Priority Pollutants*

Compound	Run No. 7 - Direct Filtration: Pilot Inf. (ppb)	Filter Eff. (ppb)	Run No. 19 - Hydroxide ppt.: Pilot Inf. (ppb)	Clarifier Eff. (ppb)	Filter Eff. (ppb)
Benzene	<10	<10	<10	<10	<10
Chlorobenzene	<10	ND[a]	ND	ND	ND
Chloroform	ND	ND	ND	ND	ND
Methylene Chloride	430	57	ND	ND	ND
Toluene	<10	<10	ND	ND	ND
Anthracene	<10	<10	<10	<10	<10
Fluoranthene	<10	<10	ND	<10	ND
Pyrene	<10	<10	ND	<10	ND
Chrysene	<10	ND	<10	ND	<10
Bis(2-ethylhexyl)-phthalate	<10	<10	<10	<10	<10
Phenol	ND	ND	ND	14	ND
2-nitrophenol	44	33	ND	ND	ND
2,4-dimethylphenol	ND	ND	<10	<10	<10
2-nitro-4-methylphenol	[b]	[b]	ND	ND	ND

[a]*Not detected.*

[b]*Non-priority pollutant compound tentatively identified but not quantitated.*

signed by incorporating input from the pilot plant operation experience with normal process design considerations. Chemical use and labor requirements were based largely on pilot plant data and operating experience.

The costs have been developed primarily as estimates for the treatment alternatives under consideration to serve as a basis from which economic comparisons of the alternatives may be made. Because of the wide diversity among individual sinter plants, generalized BAT model treatment plants were employed in developing costs. These model plants were designed as "add-on" facilities to existing BPT systems for upgrading to BAT treatment. Therefore, it is assumed that the influent wastewater to the BAT facilities was already of BPT effluent quality.

The EPA-designated model sinter plant, on which the equipment for the plants was sized and on which cost estimates were based, produces 4,000 tons of product per day and discharges 75 gallons of blowdown per ton. Thus, the design flow of 208 gpm was employed for equipment sizing and process alternative comparison. The treatment facilities were sized for continuous operation.

In developing the cost estimates, an effort was made to provide a realistic and representative estimate for implementing the BAT treatment alternatives. However, site-specific costs will influence actual costs for any facility. In addition to these site-specific costs, a few other costs have not been included. Construction cost estimates do not include:

1. Land acquisition/space allocation
2. Ancillary facilities
3. Retrofitting/process equipment adaptation
4. Equipment replacement
5. Backup facilities, except those normally engineered into wastewater treatment design
6. Utility and yard services
7. Start-up costs
8. Indirect costs (interest during construction, insurance).

Conclusions

Study Conclusions

Results of the pilot studies for treating sinter plant blowdown indicate that both direct filtration and hydroxide precipitation followed by filtration are effective in removing the selected BAT pollutants to the levels indicated in the effluent guidelines and limitations.

Direct filtration significantly reduced suspended solids, oil and grease, and heavy metals levels. A slight reduction in phenols levels was observed. None of the pollutant parameters for which effluent limitations have been promulgated exceeded these limitations.

Hydroxide precipitation followed by filtration also produced an effluent that met all limitations.

Influent cyanide concentrations and, consequently, effluent concentrations met both the maximum and average BAT limitations throughout the study. As expected, the data showed that neither process removed cyanide.

Since the pH of the influent wastewater was fairly high and good removal of metals, suspended solids, and fluoride was observed in the preclarifier, the benefits of raising the pH further by lime addition were marginal. Optimizing the clarification step in BPT, by a lower overflow rate and polymer addition, may be able to achieve an effluent quality comparable to that achieved by direct filtration.

Both treatment trains appear to be capable of providing the degree of treatment required to meet effluent limitations. Direct filtration, however, is considerably less expensive and requires less operator attention and maintenance than hydroxide precipitation followed by filtration.

Study Constraints and Limitations

The primary objective of the testing program was to develop data for alternative treatment systems as applied to sinter plant wastewater. Although the treatment processes that were evaluated in this study have been previously tested or applied for the treatment of metal plating wastewaters and other iron and steel wastewaters, no data existed for their application to the treatment of sinter plant wastewater. The EPA requested the development of 12 data points for each treatment alternative, to be accomplished by 8-hour composite sampling during 24-hour per day pilot plant operation. This approach was taken primarily because of time constraints. It is important that the results of the testing program be viewed in the proper perspective, with due consideration of the limitations attendant to both the duration and the method of testing.

Direct Filtration and Hydroxide Precipitation—The data for the two treatment

Table 5. Promulgated BAT and BPT Effluent Limitations

	Average		Maximum	
	Concentration Basis (ppm)	Effluent Limitation (kg/kkg product)	Concentration Basis (ppm)	Effluent Limitation (kg/kkg product)
Discharge (gal/ton)	75			
Total Suspended Solids	90	0.0250	275	0.0751
Oil and Grease	20	0.00501	50	0.0150
Ammonia (N)*	20	0.00501	50	0.0150
Total Cyanide	2.0	0.000501	4.0	0.0010
Phenols	0.20	0.0000501	0.35	0.0001
TRC*	--	--	0.90	0.00025
Lead	0.50	0.000125	1.5	0.000375
Zinc	0.55	0.000150	1.5	0.000450
pH	Within the range of 6.0 to 9.0			

*Ammonia (N) and Chlorine Residual (TRC) limitations were developed for the alkaline chlorination alternative only.

*Table 6. Summary of Annual Capital and Operating Costs**

Item	Hydroxide Precipitation	Direct Filtration
Construction Costs	571,500	362,900
Engineering and Construction Management, 20%	114,300	72,600
Contingency, 15% of Construction and Engineering	85,700	54,400
Total Capital Cost	771,500	489,900
Amortized Capital Cost (10 yr at 18%)	171,700	109,000
Annual Operating Costs		
Labor	70,000	70,000
Chemicals	19,000	0
Power	6,100	2,000
Maintenance (Materials and Labor)	7,700	4,900
Total	102,800	76,900
Total Annual Cost	274,500	185,900
$/1,000 gal. treated	$2.51	$1.70

*Based on third quarter of 1981.

alternatives evaluated were generated under controlled operating conditions over 4 days of operation. The test results, therefore, reflect a very limited range of influent conditions and pilot plant operating parameters. Long-term changes in the raw wastewater composition, temperature, and pH, and variations in treatment plant operation, may produce results that are different from those observed during the test period.

Bench tests were conducted with the objective of pre-establishing certain operating conditions, primarily chemical dosage and pH. However, most pilot plant operating parameters were selected on the basis of experience to give a practicable and/or reasonably conservative system, within the constraints of the existing pilot equipment. Process optimization was not attempted during the pilot plant operation.

Comparison of effluent quality achieved by each treatment alternative with the BAT limitations was based on average and maximum values for twelve 8-hour composite samples of effluent, and not 30-day average and maximum values of 24-hour composites, as would be required for permit compliance.

In summary, the pilot plant test results indicate the range of effluent concentrations achievable by the processes tested with the raw wastewater characteristics that existed at Armco Steel's sinter plant during the pilot testing period. The average and maximum effluent concentrations do not necessarily represent the levels that can be routinely achieved industry-wide by a full sized system.

Alkaline Chlorination—Alkaline chlorination followed by filtration was attempted on the Armco Steel sinter plant blowdown. The effort was terminated due to numerous problems and malfunctions relating to the sinter plant operation.

A field crew was on-site to run the alkaline chlorination testing in April 1981. During this time, Armco experienced many, sudden plant shutdowns. These unexpected shutdowns caused many operating problems at the pilot plant. In addition, due to a strike by ore handlers, Armco changed from the high lime sinter burden that is normally used (and which had been used throughout the study) to a high iron burden not normally used by the plant. As a result, representative data was not collected for the alkaline chlorination treatment train. The scheduled move of the pilot trailer to the next test site prohibited further testing at the Armco sinter plant to generate the desired data.

Recommendations

Based on limited data from this study, optimized BPT clarification to minimize overflow rates plus polymer addition followed by filtration is identified as being most advantageous for the treatment of sinter plant blowdown. This incorporates advantages of both processes—the relatively low cost of direct filtration and the flocculation and additional settling provided by the hydroxide precipitation process. It was apparent from the data that the additional metals removal provided by the hydroxide precipitation was due to a reduction in the net residual suspended solids concentration rather than the increase in pH since the concentrations of soluble metals were virtually unchanged. Additional testing of this treatment scheme would provide a more conclusive data base.

The constraints of short-term piloting should be recognized. The pilot plant data base was limited to the wastewater quality encountered at the time of the testing and the process operating conditions employed. It was not possible to develop data for a broad range of wastewater quality or to optimize process operation in the short period of pilot testing. Therefore, augmenting the existing pilot plant data base with longer term pilot studies designed to optimize treatment processes and evaluate a reasonable range of variables (or even full-scale testing) would be beneficial.

Confirming the data base on a sinter plant with an acid burden and acid blowdown would also be beneficial. Many sinter plants have a blowdown with a pH that may be as low as 2.0. In such a system, the makeup of dissolved metals would be completely different.

Conversion Factors

Although EPA policy is to use metric units in its documents, certain nonmetric units are used in this Summary for convenience. Readers more familiar with the metric system may use the following factors to convert to that system.

Nonmetric	Times	Equals Metric
ft^2	0.0929	m^2
gal.	3.785	l
in.	2.54	cm
ton	907.18	kg

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The complete report, entitled "Alternative Processes for Treatment of Sinter Plant Wastewater," (Order No. PB 85-211 258/AS; Cost: $10.00, subject to change) will be available only from:
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