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Project Summary

Toxicity Treatability of Iron and Steel Plant Wastewaters: A Resource Document

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The full report documents an assessment of the biotoxicity reduction and concurrent pollutant reduction achieved by 24 wastewater treatment systems serving 8 iron and steelmaking process subcategories. Sampling programs, designed to provide measurements before and after successive unit treatment processes, were conducted at seven plants. Chemical analyses were performed for conventional, priority, and regulated pollutants. Additional tests were made to identify other potentially harmful metals and organics. Bioassays were performed using both minnows and daphnia. The results of chemical analyses were compared with toxic concentration limits in relating biotoxicity to pollutant concentrations.

Cokemaking wastewater treatment systems tested that employed single-stage bioreaction yielded more highly toxic effluents than did the physical/chemical treatment. Ironmaking waters treated to below 2,000 μg/L total metals were nontoxic to minnows. Steelmaking waters after flocculation and clarification retained toxic levels of lead and zinc. Hot forming wastewaters showed low biotoxicity where metal concentrations were reduced sufficiently. Cold forming wastewaters showed varying biotoxicities associated with the levels of oil and grease, organics, and metals remaining after treatment. Treatment studies for hot coating and pickling wastewaters showed good reduction of biotoxicity.

This Project Summary was developed by EPA's Industrial Environmental 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

Raw wastewaters from iron and steelmaking processes have been shown to contain potentially biotoxic pollutants. Outfall compliance data identify toxicities that persist after currently applied treatments. Treatments have been assessed for removal of identified and regulated pollutants, but not for concurrent reduction of biotoxicity. As part of EPA's industry-specific toxicity information program, this study develops data on wastewater toxicity, its treatability, and its variability from eight iron and steelmaking process subcategories.

With the cooperation of the plants, wastewater treatment systems were selected to include eight iron and steelmaking process categories: cokemaking, ironmaking, steelmaking, continuous casting, hot forming, pickling, cold forming, and hot coating. Many technologies included in the treatment systems were representative, to some extent, of BPT, BAT, or NSPS. Several systems were chosen to identify possible limitations in biotoxicity removal. Each study was carried out while the production facility was operating at rates reasonably representative of normal production.

Wastewater treatment systems in steel plants are somewhat unique. While those studies use many of the unit processes inherent in BPT and BAT models, a complete match, process by process, seldom exists. Selected systems included processes that have been shown to decrease pollutant loadings.

Samples were taken upstream and downstream of treatment system unit processes. Composite samples were obtained using automatic samplers except where work areas were designated hazardous. Composites in such areas were made from a sequence of grab samples. Grab samples were also taken to prevent loss of cyanide, volatile organics, and oil and grease through degradation that might occur during composite sampling.

Containers were packed in ice for immediate delivery to testing laboratories, and were analyzed within prescribed holding periods.

Ten percent of the composite samples taken were split for chemical analyses by the two laboratories involved, for quality control purposes. All sampling and analyzing were done according to a comprehensive quality assurance plan prepared for the study.

Summary and Conclusions

Analytical results indicated that the wastewaters sampled were generally representative of their respective process subcategories. While some raw wastewaters were markedly different from median values developed previously, the overall characterizations show typical subcategory trends.

Toxicity and pollutant reductions affected by treatments were determined, and are presented in detail in the full report. Where treated wastewaters remained toxic, pollutants with remaining concentrations greater than toxic limits previously determined in other studies are given here. These are identified as probable causes. Using this method, little evidence of synergistic effects was found. That is, where several toxic pollutants remained just below their toxic limits, their combined presence did not appear to induce higher biotoxicity.

Cokemaking

Three treatment systems were studied: two using single-stage bioreaction (no nitrification), and one using physical/chemical treatment.

Plant C's bioreactor feed is first cooled and diluted with river water. The two parallel biobasins used 136 aerators. Retention time was 62 hours. Effluent was clarified after polymer addition. Toxicity (LC_{50}) to minnows was reduced from 0.61 to 3.8; daphnia EC_{50} was not reduced significantly (<1 to 1.5). Ammonia, cyanide, and benzo(a)pyrene were reduced 39, 6, and 0 percent, respectively, and all were above toxic concentrations in the treated waters.

Plant D's bioreactor feed was diluted also. Less aeration was used, and retention time was 32 hours. Bioreactor effluent passed through a thickener before discharge. Upsets in operation permitted carryover of solids, and initial toxicities were higher than those from later resamples. Toxicity to minnows was reduced from 0.17 to 32.3; for daphnia, from 0.16 to 31. Remaining biotoxicity coincides with concentrations of ammonia, phenol, benzo(a)pyrene, cyanide, and zinc that exceed toxic limits.

Plant G's treatments include equalization, clarification, filtration, carbon adsorption, and alkaline chlorination. Equalizer holding time was 24 hours; clarifier overflow, 0.0037 m^3/min; filter flowthrough, 0.045 $m^3/m^2 \times min$; adsorber flowthrough, 0.09 $m^3/m^2 \times min$; and chlorinator detention time, 2.8 hours.

Minnow LC_{50} was reduced from 0.85 to 71.5; daphnia EC_{50} was not reduced, and remained at 5.3. Residual chlorine, cyanides, and copper (extraneously introduced) all exceeded toxic concentrations in the final effluent.

Ironmaking

Plant A's recycle system uses thickeners (holding time 3.6 hours) with polymer addition and sludge recycle. Overflow passes to a cooling tower and makeup. Blowdown is clarified and chlorinated, then used for coke quench. No reduction in biotoxicity to either minnows (21.6) or daphnia (6.8) was shown. Chlorine and zinc remained above toxic limits, although the latter was 98.8 percent removed.

Plant D's treatments included flocculation and thickening, with an overflow rate of 0.03 $m^3/m^2 \times min$ at a flow rate of 56.8 m^3/min. Raw and treated waters were nontoxic to minnows; EC_{50}'s were 42 for daphnia. Ammonia, lead, and zinc exceeded criteria or toxic limits.

Steelmaking

Two treatment systems were studied at Plant A.

That for a suppressed combustion process used hydroclones, settlers, polymer addition, and thickening (5-hour holding time). Minnow LC_{50}'s were 71 on treated waters; daphnia EC_{50}'s, 58.6. Phenol, lead, and zinc were 0, 99, and 99.4 percent removed, respectively, but still exceeded toxic concentrations. Ammonia (60 percent removed) at 0.4 mg/L may have contributed to toxicity.

The system for wet open combustion used thickening after polymer addition, and pH adjustment. Blowdown passed through a second thickener. Minnows survived in a 65 percent dilution; daphnia EC_{50} was >32. Ammonia, lead, and zinc were 65, 93, and 98 percent removed, respectively, but remained above toxic concentrations.

Continuous Casting

Plant B's treatments were: scale pits, deep bed filters (walnut shells), cooling towers, and recycle. Raw and treated water were nontoxic to minnows. Daphnia were killed in a 60 percent sample. Ammonia, zinc, and copper were removed 0, 30 and 10 percent, respectively, and remained slightly above toxic limits.

Plant E's treatment included: scale pits, deep sand filters, cooling towers, and recycle. Minnow LC_{50}'s were unchanged at 2.4-2.75; daphnia EC_{50}'s remained at 6.2-6.6. Nickel, zinc, and copper were removed 7, 17, and 13 percent, respectively, but remained above toxic concentration limits.

Hot Strip and Cold Rolling Mills

Plant A treated combined hot and cold rolling wastewaters using scale pits, oil skimming, flocculation with alum and polymer, and clarification (1.6 hours retention). Then a central treatment was applied to these and waters from the slabbing mill. This included scalping with chlorination and settling basins. Minnows survived in 64 percent raw and treated, hot-forming wastewaters; daphnia showed an EC_{50} of >32. Residual chlorine may have contributed to the toxicity.

The cold rolling raw wastewater showed a minnow LC_{50} of 0.45 and a daphnia EC_{50} of 8.3. Further increases in toxicity were shown after sump waters were added. Tetrachloroethylene, lead, nickel, and zinc were reduced 0, 65, 26, and 13 percent, respectively, from their above toxic levels by treatment and dilution (31 times) with hot-forming wastewaters. After central treatment, the biotoxicities were essentially the same as those of the raw hot-forming wastewaters.

Plant D combined slabber and scarfer wastewaters with those from hot-forming, and applied oil skimming and filtration using sand and anthracite coal. Minnow LC_{50} was 35 on filtered waters; daphnia, >32. Ammonia, nickel, and zinc were removed 41, 51, and >75 percent, respectively, but remained above toxic concentration limits.

Plant F applied scale pits, settling, oil skimming, and deep-bed filtration to hot-forming wastewaters. Neither the raw nor the treated wastewaters were biotoxic. Ammonia, nickel, and zinc were removed 0, 73, and 89 percent, respectively, but their remaining concentrations slightly exceeded some toxicity limits.

Slabbing Mills

Plant A's slabbing mill wastewaters were combined with hot-strip mill waters for treatment. Raw wastewaters from the slabbing mill were only slightly toxic to minnows; the EC_{50} for daphnia could not be calculated due to inappropriate choice of dilutions for the test, but was reduced by treatment. Ammonia was not reduced and exceeded toxic limits.

Plant B applied scale pits, polymer addition, and settling basin with oil skimming. Raw and treated waters were nontoxic to minnows and daphnia. Lead and nickel were reduced 67 and 36 percent, respectively, but remained very slightly above toxic limits.

Section Mills

Plant A applied scale pits, oil skimming, clarification, dilution, and cooling. Raw and treated waters were nontoxic to minnows; toxicity to daphnia was not defined. Metals were reduced 97 percent. Ammonia remained at $<$0.4 mg/L.

Plant E applied oil skimming, cooling, and recycle, with blowdown to central treatment with combined wastewaters. The waters were not toxic to minnows and only slightly toxic to daphnia before and after oil skimming.

Pickling

Plant F (combination acids) applied neutralization, polymer addition, clarification, and dilution to raw wastewaters. Treated waters were nontoxic to minnows, and 75 percent of the daphnia survived in 100 percent sample. Ammonia and nickel were reduced 0 and 99.6 percent, respectively, but remained above toxic limits.

Plant B (hydrochloric acid) combined these wastewaters with cold-rolling waters and applied oil skimming, air oxidation, neutralization with lime, and clarification after polymer addition. Minnow LC_{50} was reduced from 8.8 to nontoxic; daphnia, from 90 percent killed in a 6 percent sample to 100 percent killed in a 95 percent sample. The pH was low after treatment. Final toxicity may have been due to additives that were not determined in the analyses.

Cold Forming

Plant A applied oil skimming, followed by a central treatment of combined wastewaters. Raw waters were nontoxic to minnows, as were treated waters. Daphnia EC_{50} was reduced only to 4.2 by treatment. High oil and grease and other organics are suspected causes of remaining toxicity.

Plant B's cold-rolling system was discussed under *Pickling*, above.

Hot Coating

Plant C applied equalization, neutralization with lime, and clarification with polymer. The effluent was nontoxic to minnows and daphnia, although zinc (98 percent removed) remained above toxicity limits.

Central Treatment

Plant E's combined waters for central treatment showed a minnow LD_{50} of 2.4 and an EC_{50} for daphnia of 0.1. Central treatment applied chrome pretreatment, cyanide pretreatment, equalization, neutralization with caustic and acid, flocculation with polymer, clarification and surface skimming. Minnows survived 65 percent in a 100 percent sample; daphnia EC_{50} was 38. Ammonia, chlorine, and nickel were reduced 0, 0, and 99.5 percent, respectively, but remained above toxic concentration limits.

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The complete report, entitled "Toxicity Treatability of Iron and Steel Plant Wastewaters: A Resource Document," (Order No. PB 84-232 495; Cost: $13.00, subject to change) will be available only from:
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