



Project Summary

Demonstration of a Maximum Recycle, Sidestream Softening System at a Petrochemical Plant and a Petroleum Refinery

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New full-scale maximum recycle sidestream softening systems at USS Chemicals, Houston, Texas, and TOSCO Refinery, Bakersfield, California, were evaluated as a technology to achieve zero wastewater discharge. Softener process efficiency was optimum at a pH control range of 10.3 to 10.5 at 40°C and using a high mixing intensity. A problem of heat exchanger biofouling from the high dissolved organics in recycle water was effectively controlled by using Bromocide with chlorine. A total organic carbon balance over the cooling water system showed raw makeup water and process water contribute 1/3 and 2/3 of the organics, respectively. Major organic sinks were drift (60%), biodegradation (30%), and volatilization (10%). Softener sludge as analyzed for chromium by leachate tests was classified as nontoxic. Heat exchanger equipment averaged two mils/year internal corrosion. External corrosion from drift aerosols was corrected by installation of a ferrous sulfate reactor in the blow down system and improved drift eliminators in cooling towers. The TOSCO water problem of high silica and low magnesium was corrected by adding caustic and magnesium sulfate to the softener. Both plants operated satisfactorily at near zero liquid discharge. Operating costs and benefits are discussed.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to an-

nounce 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

The USS Chemicals plant in Houston produces ethylene from a refinery gas rich in ethane by a steam cracking process, and manufactures styrene from ethyl-benzene by a catalytic process. The plant is medium sized, with 200 employees.

Prior to 1979, the plant discharged roughly 300 to 500 gallons per minute of effluent to the Houston Ship Channel. The wastewaters consisted primarily of oily condensates from the ethylene unit that were collected and treated in a coagulation/flocculation unit and added to the cooling water systems. The blow-down from these systems with plant runoff and demineralizer spent regeneration fluid constituted the effluent.

The regulations governing the quality of the effluent were made more stringent in a stepwise fashion starting in 1974. At that time, USS Chemicals initiated a water management study to determine the need for wastewater treatment facilities. Various schemes for upgrading the existing facilities such as biological treatment, dirty boiler, and activated carbon were compared to the sidestream softening recycle system. The study showed that the waste from other systems was not very biodegradable or adsorbable. On the

basis of economics, the recycle system was chosen. The savings in water makeup, which was from a surface water delivery system, coupled with the reality that there were no feasible alternative treatment processes, resulted in a decision to choose the current system.

The strategy for successful implementation would be quite simple. The chemical scale from constituents—calcium, magnesium, and silica—would be removed in the softener. The other ions, such as sodium, chloride, and sulfate, would be concentrated and controlled by drift, the aerosol droplets escaping with the heated air from the cooling tower. The potential problems were high total dissolved solids (TDS), which increased the corrosivity of the cooling water; concentration of non-volatile organics, which increased the biofouling potential; and external corrosion from the deposition of the drift aerosols.

The potential advantages were elimination of blowdown, which was the largest quantitative source of effluent requiring treatment prior to discharge; savings in makeup water; and a way to continue to use chromate corrosion inhibitors. Hexavalent chrome was found to be toxic at low concentrations so that regulations called for nearly complete removal. At that time, there were no equivalent substitutes for chromate as a corrosion inhibitor.

Pilot testwork of the proposed system was conducted in 1974-75. Construction began in 1977 and coincided with the conversion from ground water to surface water supply. The entire facility, including surface water treatment units, had a capital cost of roughly \$3 million of which half the cost was for the sidestream softening system.

This system was unique in a number of ways. First, carbon dioxide instead of sulfuric acid was used to control pH in the cooling water system. The reasoning was that carbon dioxide preserved the bicarbonate in the raw water, and thus greatly reduced the need for soda ash in the sidestream softeners. Sulfuric acid would have destroyed the bicarbonate by converting it to carbon dioxide that was strippable in the cooling towers. Another important reason for carbon dioxide usage was that the pH in the cooling water could only go as low as approximately four in the event of operator error or equipment malfunction, while sulfuric acid overdose could bring the pH significantly lower and damage the heat exchangers, which were of carbon steel with some stainless material.

All process water was collected, treated (if necessary), and used as makeup to the cooling water system. This included oily condensates which were treated in an API separator and a coagulation/flocculation process, boiler blowdown, and plant runoff including storm water. The only discharge was the high TDS demineralizer-regeneration water. Prior to this project, the effluent discharge was in the range of 300 to 500 GPM; afterwards, it was 30 to 50 GPM, a ten-fold reduction.

Study Objective

The objectives of the study were as follows:

1. evaluate the performance of the sidestream softening system;
2. determine the impact of the recycle streams on the cooling water system;
3. discover the fate of the organic matter in the cooling water system; and
4. investigate the potential sludge disposal problems.

Findings

1. Performance Evaluation

Prior to startup, there were two important questions. First, was there sufficient magnesium in the raw water to adsorb the silica in the softening reactions? The silica-to-magnesium ratio in the raw water was two to one (in mg/L), which was marginal. In the reaction, magnesium is precipitated as a hydroxide onto which the silica is adsorbed. The question was answered in the affirmative. As part of the project, a detailed scientific delineation of the adsorption phenomena was made.

The second question involved the selection of the appropriate scale inhibitor for the cooling water. An inhibitor was needed that worked well in the cooling water but did not significantly interfere with the softening reactions. Generic phosphonate inhibitors were found in laboratory tests to work too well in that the efficiency of the softening reactions was decreased. Selected were polymaleic anhydride polymers which mechanistically prevented scale formation by fluidizing small crystals rather than inhibiting crystal formation. That is what actually happened. The inhibitor helped maintain a scale-free heat transfer system.

The most critical element of the sidestream softening system was the softener.

Operational costs were related to the consumption of soda ash and lime in the softening process as was process efficiency. So it was important to develop the optimum control strategy for the system.

The lime dosage controlled the pH of the reaction in the softener. Soda ash was used to make up for any deficiency in carbonate in the reactor. With the use of carbon dioxide in the cooling water system, the bicarbonate in the makeup water was conserved so that the soda ash requirement was minimized. The operators were instructed to control pH within a narrow band by lime addition, and to add soda ash based on the difference between the calcium hardness and carbonate alkalinity run every four hours.

The objective of this part of the performance evaluation was to define the most cost-effective pH in the softeners with quality constraints in the cooling water. The interactions were as follows. A higher pH required a greater lime dosage and increased the soda ash usage as more carbonate was necessary to react with the calcium ions in the lime. However, the higher pH improved reaction efficiency by conversion of a greater percentage of bicarbonate to carbonate and precipitation of magnesium. Thus, for a greater cost, the benefit was a higher reaction efficiency, which allowed for a decreased flow requirement through the softeners. The optimization studies performed in the laboratory then in the plant indicated that the control pH range was 10.3 to 10.5 at 40°C.

The next performance problem analyzed was the effect of mixing intensity on the softening reactions. The softeners were manufactured by Infilco Degremont under the Densator brand name. Of particular interest was the mixing in the primary reaction zone.

Originally, a blade arm rotating on the same shaft as the bottom scraper provided slow speed mixing. It appeared to be inadequate; so two high-speed turbine mixers replaced the blade in one softener while the other softener retained the blade for comparison purposes.

The results of the testing indicated that mixing intensity was, indeed, an important variable. At low mixing intensities, the reaction/adsorption process involving magnesium precipitating as the oxide and the subsequent adsorption of silica was adversely affected. Also the lime dosage was much greater because its dissolution was strongly influenced by mixing. At very high mixing intensities, the clarification process was hindered by the breakup of the particles. Thus, an optimum mixing

intensity with the turbine mixers was defined.

Two other observations are worth noting: with the slow-speed blade it was difficult to control the addition of lime and soda ash to the softeners because the reaction zone was not well mixed, which created sampling errors, inaccurate test results, and high feedback control noise. Also, silica adsorption in the reactor was much higher than previously predicted in laboratory studies.

2. Impact of Recycled Water

The recycle water that had a strong negative impact on the cooling water system was the process wastewater which was high in dissolved organics. After the startup and shakedown of the sidestream softening system, the major unresolved problem was biofouling in the heat exchange system. It was particularly bad on the critical surface condensers. The problem was exacerbated by the operation conditions in the cooling water system. As previously mentioned, carbon dioxide was used to maintain pH control. To minimize the use and expense of the gas, which was readily stripped out in the cooling tower, the pH was maintained between 7.6 and 7.8. Chlorine was used as the primary biofouling control agent. At the higher pH, chlorine was relatively ineffective, as it was largely in the hypochlorite ion state. Thus, a research effort was undertaken to resolve the problem. An organic compound, dichlorodibromo dydantoin (trade name Bromocide) was added in conjunction with chlorine. The combination of these chemicals proved to be very effective in controlling biofilm development at a reasonable cost. The key was bromine which, when released in solution as hypobromous acid, was an effective biocide at the higher pH.

3. The Fate of Organics

A total organic carbon balance was made over the cooling water system to determine the sources and sinks of the organic material. Samples were analyzed for biodegradability. The results indicated that the raw makeup water and the process water contribute one-third and two-thirds of the organic materials, respectively. The major sinks were drift (60%), biodegradation (30%), and volatilization (10%).

4. Sludge Disposal

The most serious potential problem with the sludge from the softeners was

the classification, i.e., whether it was considered toxic and had to be disposed of in a Class 1 site at high cost. The only constituent of concern was chromium used in the cooling water system as a corrosion inhibitor. A fraction of it degraded from a hexavalent form to a trivalent form that precipitated as a hydroxide in the softeners.

A series of leachate tests were performed using both the EPA Standard and State of Texas procedures. Under a variety of conditions at the plant and in the lab, the sludge met both the EPA and State criteria. The sludge was consequently classified as non-toxic.

Other Investigations

After startup, the cooling water system equilibrated at a total dissolved solids (TDS) level between 20 and 30,000 mg/L. This figure was much higher than originally anticipated. Internal corrosion in the heat exchange equipment was never a problem, averaging below two mils per year during the course of the study. However, external corrosion caused by the deposition of drift aerosols by surrounding equipment was a real concern. As part of the study, an emergency blowdown system consisting of a reactor in which ferrous sulfate was added to precipitate the chromate and a clarifier was tested in the laboratory. As a result of the tests, a full-scale treatment system was placed into operation. Also, the major cooling tower was rebuilt with improved drift eliminators to minimize the deposition.

Summary—USS Chemicals

The sidestream softening concept was particularly attractive to USS Chemicals because the cost of their water was relatively high and their effluent discharge regulations were tough. The system is continuing to operate in a steady-state mode, achieving the original expectation with a minimum discharge.

TOSCO

At TOSCO, different reasons existed for considering zero discharge, sidestream softening. In the past the effluent had been discharged into a percolation field from which it migrated into an underground aquifer. As regulations stiffened, the discharges were shifted to an injection well system at the refinery. The injection well was costly to operate, and was taxed by the State as a hazardous waste.

Since the cooling water blowdown was a major volumetric constituent in the

injection well, it made economic sense to look for alternative ways to deal with it. In the mid-1970's several studies favorably evaluated sidestream softening for the blowdown. In 1980, the decision to proceed with that design was made.

The unique problem with the TOSCO water was its high silica and low magnesium content. Insufficient magnesium was present in the makeup water to have much adsorbing power for the silica. An evaluation of alternative ways to overcome the problem indicated that the best way was a combination of caustic as the source of hydroxide in the softener and magnesium sulfate as the source of soluble magnesium for silica reduction.

Laboratory studies had shown that magnesium in a soluble form had roughly an order of magnitude greater adsorbing power for silica than solid forms such as magnesium oxide and dolomitic lime. Caustic was attractive as a way to minimize sludge production and soda ash usage.

The system consisted of dual Densator softeners, sulfuric acid pH control tank, and dual media filters. The sludge was concentrated and pumped to a series of lined evaporation ponds.

The refinery consisted of five cooling water systems with a combined recirculation rate of 53,000 gpm, tied together. Design flow through the sidestream softener was rated for 250 gpm, of which 150 was from the cooling water system, and the remainder from the boiler blowdown and scrubber system.

Operation and Economics

Startup commenced smoothly in March 1982, with the system running at steady state within one week. A dense sludge was quickly established in the softeners. Silica was controlled to below 150 mg/L in the cooling water system by the measured addition of dissolved magnesium. The total dissolved solids level fluctuated between 5,000 and 8,000 mg/L.

Reuse of cooling water saved TOSCO roughly \$36,000 in actual water costs. Another \$300,000 was saved in supply well maintenance, power, and taxes. Water treatment chemical savings of \$50,000 were also realized. Overall, savings for the refinery were estimated at \$500,000 per year. The cost of the sidestream softening system was \$2.5 million. The capital payback period is five years.

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Donald Kampbell is the EPA Project Officer (see below).

The complete report, entitled "Demonstration of a Maximum Recycle, Sidestream Softening System at a Petrochemical Plant and a Petroleum Refinery," (Order No. PB 85-121 044; Cost: \$19.00, subject to change) will be available only from:

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★ U.S. GOVERNMENT PRINTING OFFICE: 1985 — 559-016/7885

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