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Chemical Technology Division

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ABSTRACT

The Waste Management Operations Division at Oak Ridge National Laboratory recently modified the design of a reactor/clarifier at the Nonradiological Wastewater Treatment Plant, which is now referred to as the Process Waste Treatment Complex—Building 3608, to replace the sludge-blanket softener/clarifier at the Process Waste Treatment Plant, now referred to as the Process Waste Treatment Complex–Building 3544 (PWTC-3544). This work was conducted because periodic hydraulic overloads caused poor water-softening performance in the PWTC-3544 softener, which was detrimental to the performance and operating costs of downstream ion-exchange operations. Over a 2-month time frame, the modified reactor/clarifier was tested with nonradiological wastewater and then with radioactive wastewater to optimize softening performance. Based on performance to date, the new system has operated more effectively than the former one, with reduced employee radiological exposure, less downtime, lower costs, and improved effluent quality.

1. INTRODUCTION

The Waste Management Operations Division (WMOD) operates facilities at Oak Ridge National Laboratory for treatment of wastewater containing radiological and hazardous pollutants. The effluent wastewater must meet the discharge criteria defined in a National Pollutant Discharge Elimination System permit and in U.S. Department of Energy Order 5400.5, "Radiological Protection of the Public and Environment." The Process Waste Treatment Complex—Building 3544 (PWTC-3544) removes radioactive strontium-90 (^{90}Sr) and cesium-137 (^{137}Cs) from approximately 70 million gallons per year of wastewater, using chemical softening and ion exchange. The Process Waste Treatment Complex—Building 3608 (PWTC-3608) removes heavy-metal and organic pollutants from approximately 170 million gallons per year by using chemical precipitation, air stripping, and activated carbon. The effluent wastewater from the PWTC-3544 is further treated at the PWTC-3608 for removal of trace organic components. The operating capacity and efficiency of the PWTC-3544 were limited by

the softener/clarifier system, which was undersized and sometimes troublesome to operate. The PWTC-3608, however, was designed for much higher wastewater flow rates and had redundant capacity for chemical precipitation and clarification of wastewater. With improved administrative control of pollutant discharges, segregation of wastewaters, and reduced quantities of heavy-metal discharges from generator sources, the two reactor/clarifier units at the PWTC-3608 were underutilized. In September 1993, a design study was completed that examined the feasibility of using one of the two PWTC-3608 reactor/clarifiers as a softener for the radiological process wastewater.[1] This approach reduced costs by avoiding construction of a replacement softener/clarifier at the PWTC-3544 and furthered the goal of consolidating all process wastewater treatment operations at one facility, which would significantly reduce operating costs. The treatment capabilities of the PWTC-3608 reactor/clarifier were improved by addition of a flocculation tank and a sludge-recycle system for enhancing the softening reaction. This report describes the startup, optimization, and performance evaluation for this system.

2. BACKGROUND

To improve the efficiency of ^{137}Cs and ^{90}Sr ion-exchange operations at the Process Waste Treatment Plant, the wastewater is softened in a sludge-blanket clarifier, L-1, to reduce the hardness from 150–200 mg/L $CaCO_3$ to 6–10 mg/L. WMOD personnel observed that periodic hydraulic overloads caused poor performance in the L-1 clarifier. Since the reactor/clarifiers (F-1006 and F-1007) at the PWTC-3608 were being operated at only a fraction of their design capacity, WMOD decided to use one of these, F-1006, to soften the feed to the PWTC-3544, providing enough softening capacity to handle periods of high demand. The reactor/clarifier effluent is sent to the PWTC-3544 for removal of radioactive contaminants using ion-exchange columns. The effluent from the PWTC-3544 is then sent back to the PWTC-3608 for removal of any organic contaminants.

3. PROCESS CHEMISTRY

The softening process is a series of reactions initiated by pH adjustment to 11.5. The primary effect of the hydroxide is to convert bicarbonate ions to carbonate, thus precipitating calcium as $CaCO_3$. The second effect is to precipitate magnesium as $Mg(OH)_2$. The softening process also removes about 70% of the ^{90}Sr from the wastewater and most other heavy metals that may be present.

4. SYSTEM DESCRIPTION

A simplified schematic of the F-1006 clarifier system is shown in Fig. 1. The process feed enters the system into a 975-gal flash mix tank (F-1060), where the pH is adjusted to 11.5 with sodium hydroxide and ferric sulfate is added as a flocculant. The waste then flows to a 10,000-gal flocculation tank (F-1070), where Betz 1100 polyelectrolyte (Betz Laboratories, Trevose, Pennsylvania) is added. Solids are then settled in a 60,000-gal reactor/clarifier (F-1006), with approximately 10% of the flow being recycled from the sludge layer back to F-1070. To reduce possible post-precipitation problems, the effluent pH is adjusted to between 6 and 10 before being pumped to PWTC-3544 for ion- exchange treatment. The system is monitored and controlled inside Building 3608 from a distributed control system.

5. EXPERIMENTAL PLAN

The experimental plan focused on determining the chemical and mechanical parameters that would optimize the removal of water-hardness components from the wastewater prior to ion-exchange treatment at Building 3544. The primary variables to be optimized included flow rates (and therefore concentrations) of ferric sulfate and Betz 1100, recycle flow (0 to 35 gal/min), mixer speed in tank F-1070 (0 to 50 rpm), and sludge-withdrawal rate. The system was initially started with nonradiological wastewater for equipment checkout and leak tests.

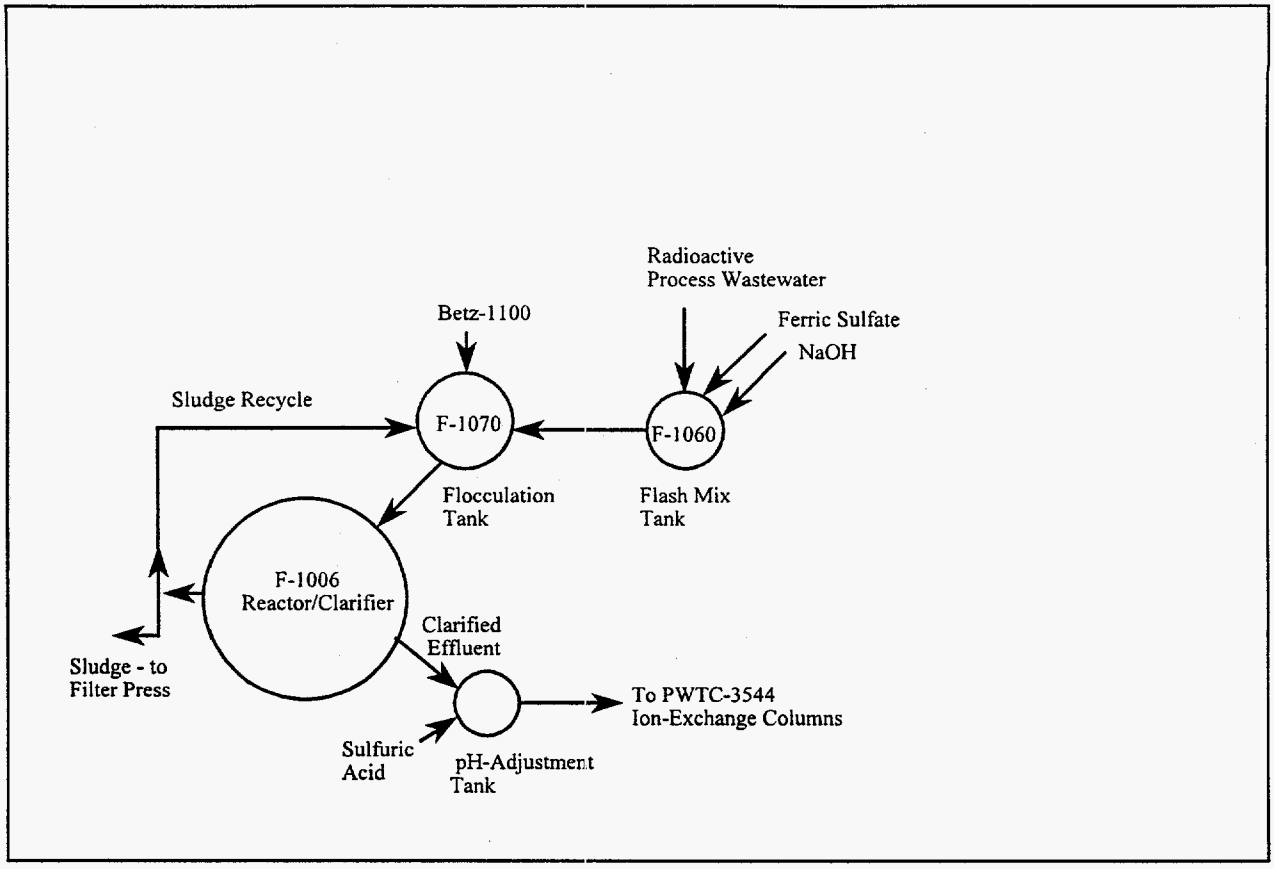

Fig. 1. Schematic of the reactor/clarifier system at Building 3608.

6. ANALYTICAL TECHNIQUES

Samples from the influent, tank F-1060, tank F-1070, the sludge-recycle line, and the clarifier overflow (F-1006) were taken to determine pH and hardness. The influent was also checked for alkalinity, and the sludge recycle was periodically checked for total suspended solids. Hardness was determined by titration with EDTA to an Eriochrome Black T end point, which measures the concentrations of calcium and magnesium, expressed as milligrams of $CaCO_3$. Alkalinity was determined by titrating with HCl (phenolphthalein and bromocresol green indicators), pH was measured with a pH meter, and total suspended solids was determined by filtration and drying.

7. RESULTS

7.1 Flocculant-Tank Mixing Tests

During initial leak testing and equipment checkout, a series of experiments was conducted to determine static mixing times for tank F-1070 at various mixer speeds. A spike of sodium chloride was added to the water in the tank, and the conductivity of the solution was monitored over time. The purpose of these experiments was to determine mixer speeds that would completely mix the tank contents in less than one-fifth the hydraulic residence time during operation. This would ensure complete mixing of all reagents before they entered the clarifier. The results of these experiments indicated that at least 20 rpm was necessary for a flow rate of 150 gal/min and that 30 rpm was necessary for flow rates of 300 gal/min. (Hydraulic residence time at 300 gal/min is 33 min.) Figure 2 shows static mixing times determined in these tests as a function of stirrer speed. Based on this information, the stirrer speed was set and left at 30 rpm for the rest of the tests to allow time and effort to be focused on other issues.

7.2 Reagent Delivery

As initial testing with nonradioactive water began, it immediately became apparent that the reagent-delivery systems were not functioning as designed. The ferric sulfate pumps (constant-volume pumps) failed periodically and did not maintain desired flow rates. The pumps, which were installed above the supply tank and were pulling 6 ft of suction lift before pumping the solution through about 180 ft of tubing to the process, were overloaded. Relocating the pumps to eliminate the suction lift solved this problem.

Additional difficulties were encountered with the Betz 1100 polymer-delivery system. Overpressure protection valves for the polymer pumps leaked to such an extent that accurate

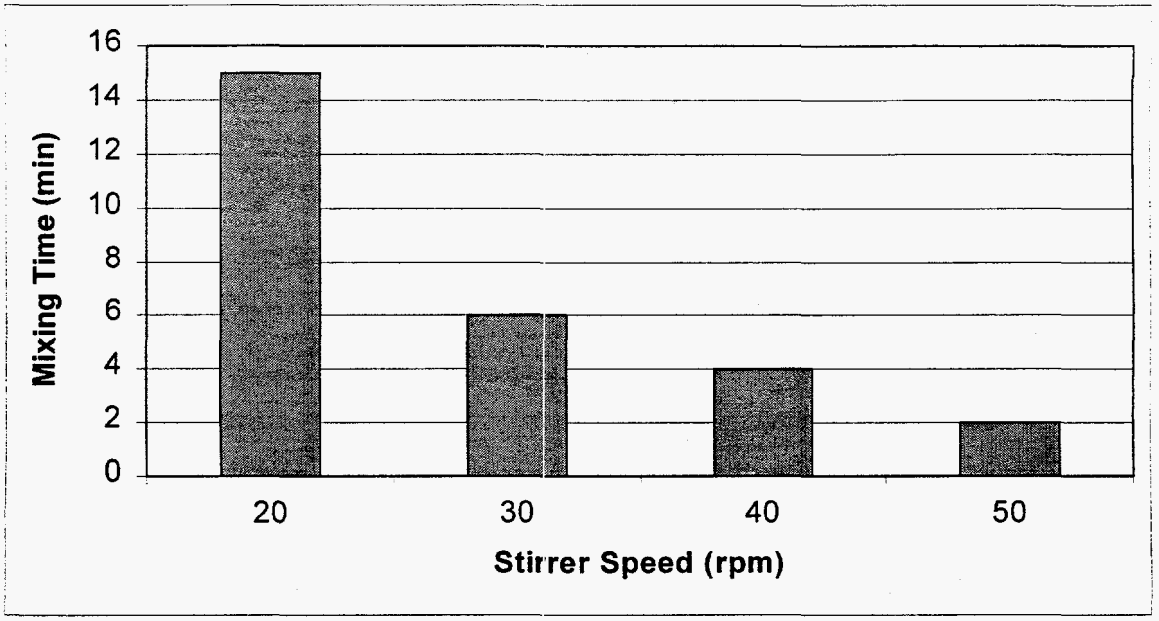

Fig. 2. Mixing time vs stirrer speed for F-1070 tank.

determination of polymer flow to (and therefore polymer concentration in) the system was impossible. On inspection, it was found that the discharge line from the valves was plugged and that polymer was leaking onto the floor. The valves had been installed in such a manner that any discharge from them had to travel upward back to the polymer tank. This left polymer in the line after a discharge, which solidified and plugged the line. The valves were relocated so that their discharge traveled downward to the polymer tank, eliminating plugging. Repairs were also made to the valves to ensure that they did not discharge as easily.

A second issue related to proper makeup of the polymer. Prior to this upgrade, the clarifier had been run in a batch mode. Batches of polymer were made up in the polymer feed tank prior to the start of a run, and the run ended when the polymer supply was depleted. The new system runs continuously, so polymer batches are made up more often, with less time for mixing. (Polymer powder takes at least 1 h to dissolve and must be carefully added to the water to avoid forming clumps, which take much longer to dissolve.) To ensure ample time for the polymer to

mix and dissolve, a polymer premix tank was added. Concentrated polymer is made up in the premix tank and sent to the polymer feed tank when needed. A large sifter was obtained, which can be used to distribute the polymer powder evenly in the premix tank and reduce clumping.

7.3 System Performance

During initial checkout with nonradioactive water, the effluent hardness varied widely. Much of the poor performance was due to pump failures and other equipment malfunctions. During early testing, the ferric sulfate pumps failed, and the sludge-recycle pumps regularly shut down due to high discharge pressure. After each problem was corrected, several days was required for the system to recover. Figure 3 shows the effluent hardness from the system during tests with nonradioactive wastewater. After the operational difficulties were corrected, the hardness concentration in the clarifier effluent was still higher than desired. Bench-scale tests on the nonradioactive water showed that a slight deficiency in carbonate was preventing optimum reductions. Several 50-lb bags of soda ash were purchased and added to the influent of the system over several days. This reduced the effluent hardness from about 70 mg/L to 30 mg/L. The tests with nonradioactive wastewater were discontinued to make final preparations for treating radioactive wastewaters.

After the feed to the system was shifted to radioactive wastewater, the effluent hardness fell to below 10 mg/L over a period of 2 weeks. When the flow rate of the ferric sulfate was inadvertently reduced, the hardness quickly rose to about 30 mg/L. The flow rate of the ferric sulfate was readjusted, and the effluent hardness fell to below 10 mg/L in about a week. The hardness tends to rise when a process upset occurs and then falls when it is corrected. Figure 4 shows the effluent hardness from the start of processing radioactive wastewaters on 5/1/97 through 7/31/97.

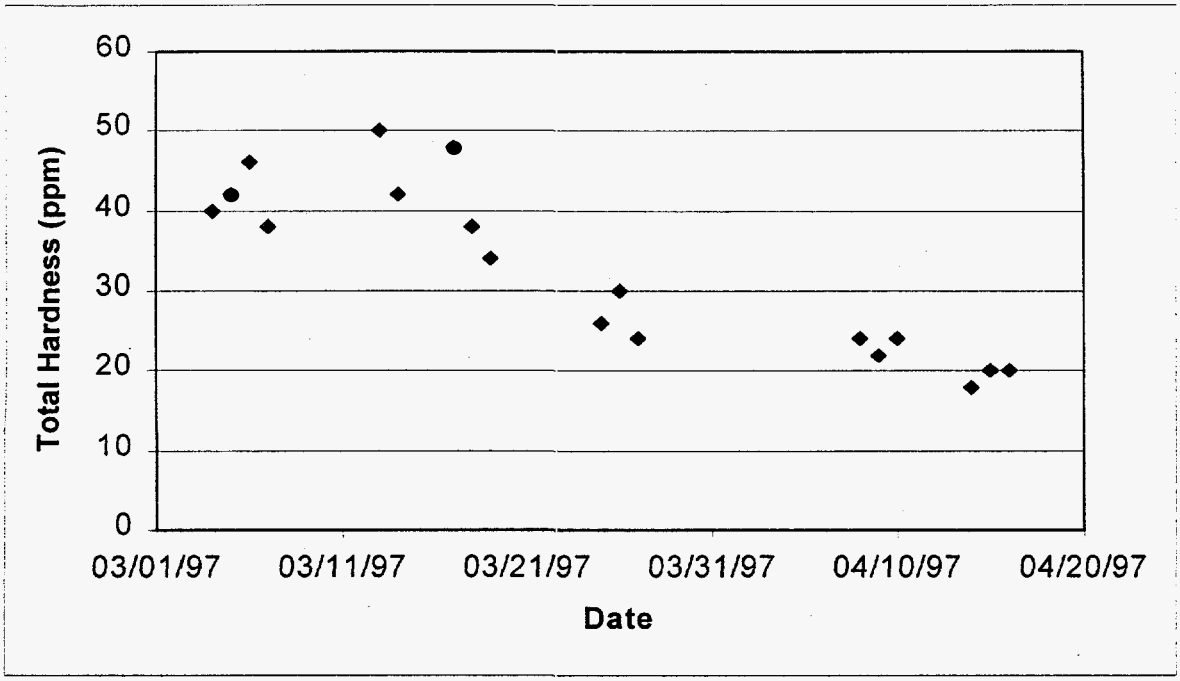

Fig. 3. Total hardness concentration for effluent from F-1006 reactor/clarifier during treatment of nonradioactive process wastewater.

Several operational parameters were not optimized for the reasons listed below; however, the system performance remains excellent. The sludge-recycle rate remains at 30 gal/min (close to its maximum of 35 gal/min) because the recycle line tends to plug with solids if the flow rate is reduced. Since the system functioned well with the stirrer speed set at 30 rpm, other speeds were not tested, and it was left unchanged. The ferric sulfate flow rate is set to produce a concentration of 5 mg/L. Several bench-scale tests have confirmed that higher concentrations do not significantly improve performance, but full-scale tests at higher concentrations were not performed. The polymer concentration remains at 2.5 mg/L. Both the sludge-withdrawal rate and the set point of the final effluent pH are adjusted by WMOD personnel as necessary.

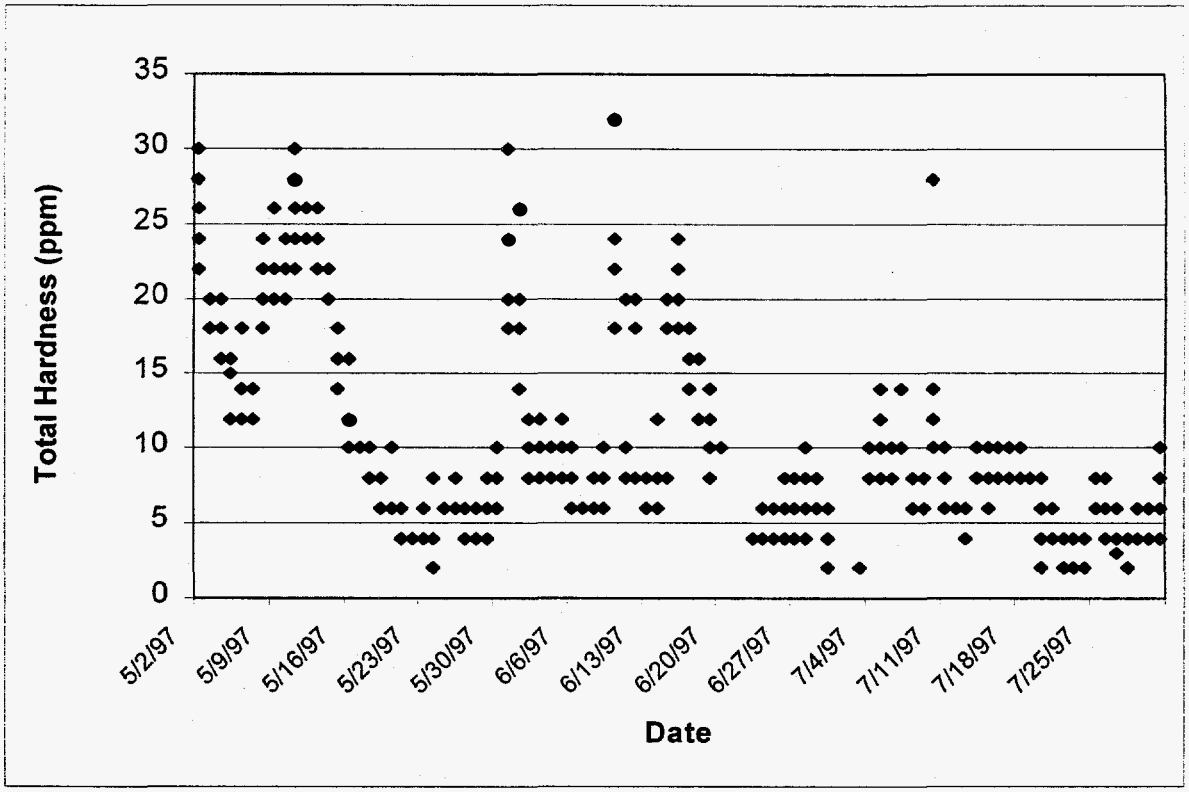

Fig. 4. Total hardness concentration for effluent from F-1006 reactor/clarifier during treatment of radiological process wastewater.

Since the test period ended, the system has been operating for almost a year without any major problems. The sludge-recycle line requires cleaning periodically, and the line between the flocculation tank and the reactor/clarifier has been cleaned once. The acid-addition pumps were recently replaced with slightly larger pumps. The hardness concentration in the clarifier effluent has typically ranged from 2 to 6 mg/L. Because of the low concentration of calcium and magnesium in the softened wastewater, the ion-exchange columns at the PWTC-3544 are more efficient. The average ^{90}Sr in the effluent from the ion-exchange columns has been reduced from 10 to 1 Bq/L. The amount of water that can be treated by the ion-exchange columns before regeneration is required has increased significantly, which reduces the amount of liquid low-level waste produced at the PWTC-3544. The average throughput was 1,183,400 gal before the change to the new clarifier system and 1,504,300 gal after, an increase of 27%.

8. CONCLUSIONS

The reactor/clarifier at Building 3608 has been consistently reducing the hardness of the influent from 160–200 mg/L to below 10 mg/L at a variety of flow rates. Several problems of a mechanical/processing nature that were affecting the operation of the system were resolved during the test period. The system has been operating routinely for over a year, with only minor problems. The hardness concentration in the effluent from the new clarifier is lower than it was with the old softener, which has improved the operation of the ion-exchange columns at the PWTC-3544 and reduced the amount of secondary waste produced.

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