Investigations of Water Treatment Processes for the Removal of Organic Matter from Sparrowfoot Quarry Water, Clinton, Missouri

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Introduction

The Henry County Water Company proposed to construct a new water treatment facility utilizing water from the Sparrowfoot Quarry near Clinton, Missouri. The quarry, initially mined for limestone, was closed prior to the completion of the Harry S Truman dam. Creation of the Harry S Truman reservoir flooded the quarry, resulting in the storage of a large volume of water of relatively constant quality and temperature.

The present series of studies of treatment processes for the removal of organic compounds in Sparrowfoot Quarry water was planned and conducted during the period 6-10 January, 1997. Henry County Water Company had received a memorandum from the Missouri Department of Natural Resources (MDNR Division of Environmental Quality, Public Drinking Water Program, by Terry Timmons, Chemical Monitoring Coordinator, Planning and Monitoring Section, December 19, 1997) advising them on the projected timetable for sampling and controlling total trihalomethanes (TTHM) in surface water supplies statewide, including those groundwater supplies considered to be under the influence of surface waters (GWUI). It is likely, therefore, that the reduction of total organic carbon (TOC) and TTHM will be required during the lifetime of the proposed new water treatment facility.

Composition of Sparrowfoot Quarry Water

Compared with the water quality of the South Grande River supply which serves the fifty-year-old water treatment plant at Clinton, Missouri, the Sparrowfoot Quarry offers significant advantages. Most important, the quarry water is far less variable in physical and chemical characteristics. Turbidity is low and near constant. Water temperatures vary only about 6°C throughout the year. Algal growth is expected to be minimal in the darkness of the quarry. Dissolved oxygen was found to be abundant (6 to 7 mg O_2/l) in the sampling conducted for the current study.

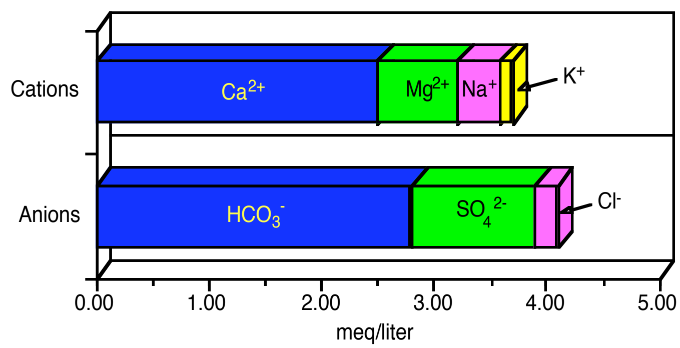
Total dissolved solids, including hardness, in the quarry water was found to be about one-half that of TDS observed in the South Grande River water (MDNR data, January 10, 1996). Sulfate ion in the quarry water was one-quarter the concentration recorded for the South Grande River.

A comparison of the electroneutrality conditions (ion balances) is shown for both the Sparrowfoot Quarry and South Grande River waters in Figure 1. These bar diagrams show the hardness of the Quarry water is less than one-half that of the River water. However, the lack of a cation-anion balance indicates that some ionic constituents of the quarry water were not fully accounted for. There is a 10% discrepancy in the ion balance for the Quarry water.

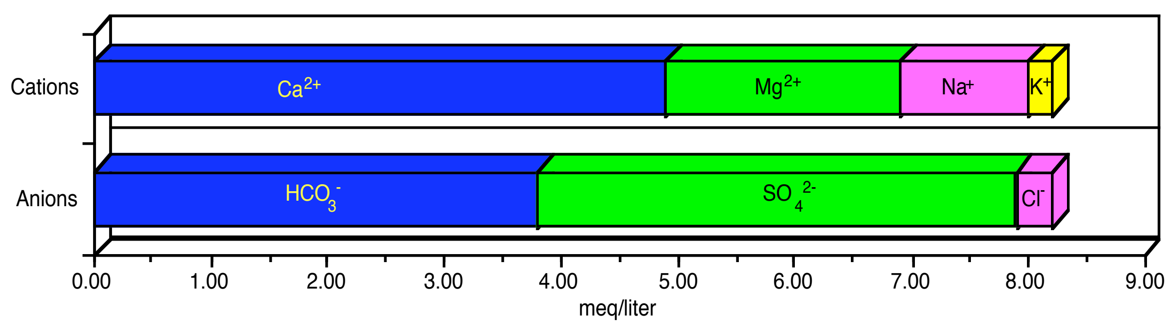
The presence of oxygen indicates that treatment for oxidation of reducing agents (ferrous ion, manganous ion, hydrogen sulfide, ammonium ion, nitrite ion) may not be necessary. In addition, the lower hardness should be a significant benefit to most household water users.

Figure 1. Electroneutrality Conditions for Sparrowfoot Quarry and South Grande River Waters

Sparrowfoot Quarry Water



Henry County Water Company - South Grande River Water



1 meq / l = 50 mg $CaCO_3$ equivalent / l

Proposed New Water Treatment Process

The Henry County Water Company retained Larkin Associates to design the new treatment facility in Clinton. By January 1997, a preliminary design had been completed, as shown in Appendix A. The treatment plant proposed by Larkin Associates includes the following processes intended for the reduction of turbidity and the removal of organic matter:

Stage 1. The addition of powdered activated carbon (PAC) in a flow-through contact basin. This will provide 25 minutes detention at a design flow of 3 mgd. (An objective of this study was to determine the dose-response of PAC in removing organic matter from the source water under this treatment condition.)

Stage 2. The addition of liquid filter alum plus sulfuric acid in a rapid mix basin to depress pH to enhance removal of TOC . At the lowered pH, the added alum should still be capable of forming an aluminum hydroxide floc. (An objective of the current study was to determine the extent to which the alum floc formed in the rapid mix basin removed organic matter in the quarry water.)

Stage 3. The addition of lime (CaO) for neutralization of pH in a second rapid mix stage immediately prior to solids removal in an upflow solids contact basin.

Stage 4. The removal of precipitated solids in an upflow, pulsed bed solids contact basin (Infilco Degremont 'Pulsator'). The sludge blanket in the upflow contact basin is intended to provide additional contact time for the PAC so that the adsorption capacity of the PAC is completely utilized.

Simulation of the Proposed Treatment Process

A series of experimental bench-scale (jar test) studies were designed in an effort to determine the effectiveness of alternative coagulants, lowered pH and the addition of PAC on achieving 'enhanced coagulation' for increased removal of organic matter from Sparrowfoot Quarry water. In particular, efforts were made to simulate the design treatment process for the proposed new water purification plant. Control and treated samples were taken in these studies to determine the degree of removal of TOC and the concurrent reduction in TTHM formation potential (TTHMFP). In addition, turbidity reduction, pH, and alkalinity were monitored through the process.

The first series of three studies was directed at determining the optimum coagulant dose for conventional water treatment using three types of alum. The second test series employed this optimum alum dose in conjunction with varying dosages of PAC to determine the dose-response to PAC addition.

The third series of tests was to simulate the proposed new treatment plant design process. After PAC addition, alum was applied at low pH to achieve conditions representative of 'enhanced coagulation'. Prolonged flocculation was used to simulate the agitation of alum floc plus PAC in the sludge blanket.

Laboratory Studies

I. Determination of Optimum Alum Dosage for Removal of Suspended Matter

The first three series of jar test studies were conducted using three candidate coagulants (standard liquid alum solution, liquid alum with 4.6% sulfuric acid added, and liquid alum with 9.6% sulfuric acid added). From these studies, the optimum coagulant dosage for turbidity reduction was selected. While effective turbidity reduction was achieved at all coagulant dosages in the range of 20 - 60 mg/l, 40 mg/l was selected as the optimum dosage for all three coagulants tested.

These studies simulated conventional coagulation. PAC was not applied in this first series of tests. The influence of the coagulant additions on alkalinity, settled water turbidity, and pH arepresented in Table 1 and shown on Figures 2-4.

Table 1. Determination of Optimum Liquid Alum Dosages (with 0%, 4.7%, and 9.6% Sulfuric Acid) for Reduction of Turbidity in Sparrowfoot Quarry Water

Standard Liquid Alum, mg/l	**0**	**10**	**20**	**30**	**40**	**50**	**60**
Turbidity (ntu)	15.6	9.73	1.16	0.51	0.35	0.34	1.29
pH	7.8	7.7	7.6	7.5	7.4	7.3	7.2
Alkalinity, mg CaCO3 equiv./l	108	100	96	90	84	76	70

Liquid Alum + 4.7% sulfuric acid	**0**	**10**	**20**	**30**	**40**	**50**	**60**
Turbidity (ntu)	15.9	13.3	1.35	0.58	0.41	0.40	0.44
pH	7.7	7.7	7.6	7.6	7.5	7.3	7.1
Alkalinity, mg Ca CO3 equiv./l	108	96	90	80	72	68	58

Alum + 9.6% sulfuric acid	**0**	**10**	**20**	**30**	**40**	**50**	**60**
Turbidity (ntu)	15.3	17.2	1.71	0.75	0.77	0.65	0.89
pH	7.8	7.7	7.6	7.4	7.3	7.2	7.1
Alkalinity, mg Ca CO3 equiv./l	104	94	84	79	66	58	46

Figure 2.

Determination of Optimum Alum Dosage using Alum with 0%, 4.7% and 9.6% Sulfuric Acid Sparrowfoot Quarry Water, Clinton, Missouri, January 7, 1997

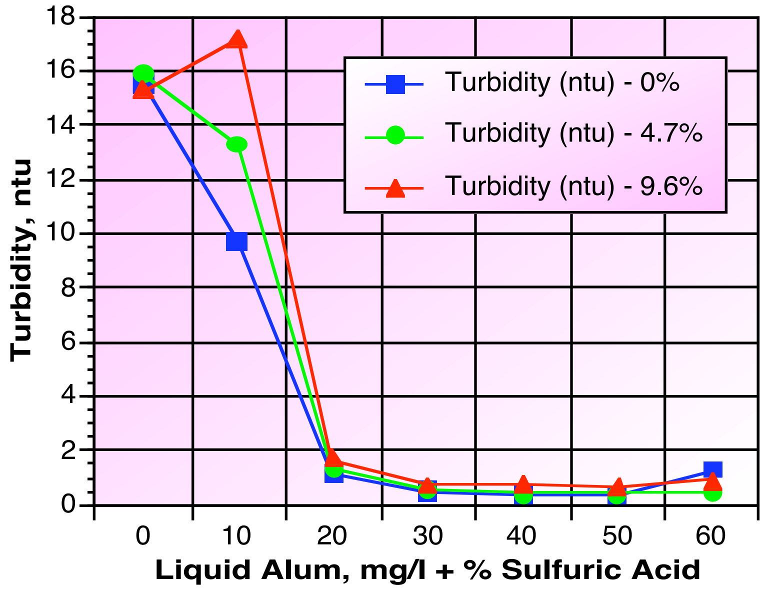


Figure 3.

Effect of Optimum Alum Dosage using Alum with 0%, 4.7% and 9.6% Sulfuric Acid on pH of Sparrowfoot Quarry Water, Clinton, Missouri, January 7, 1997

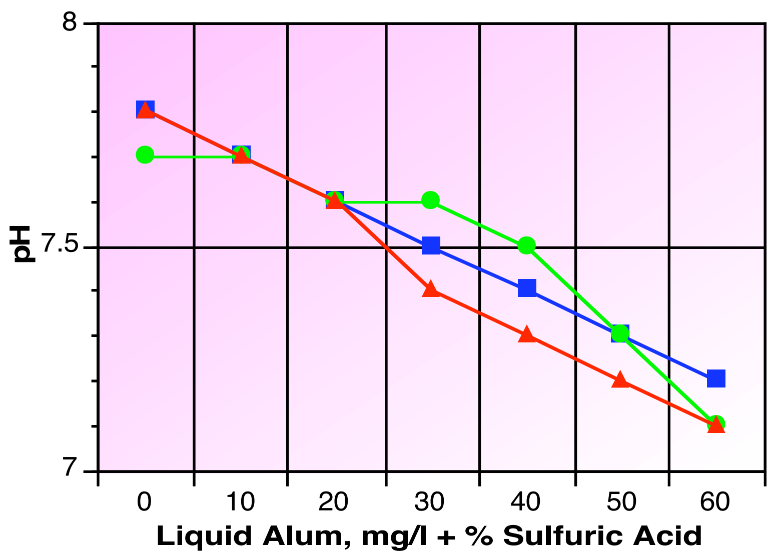
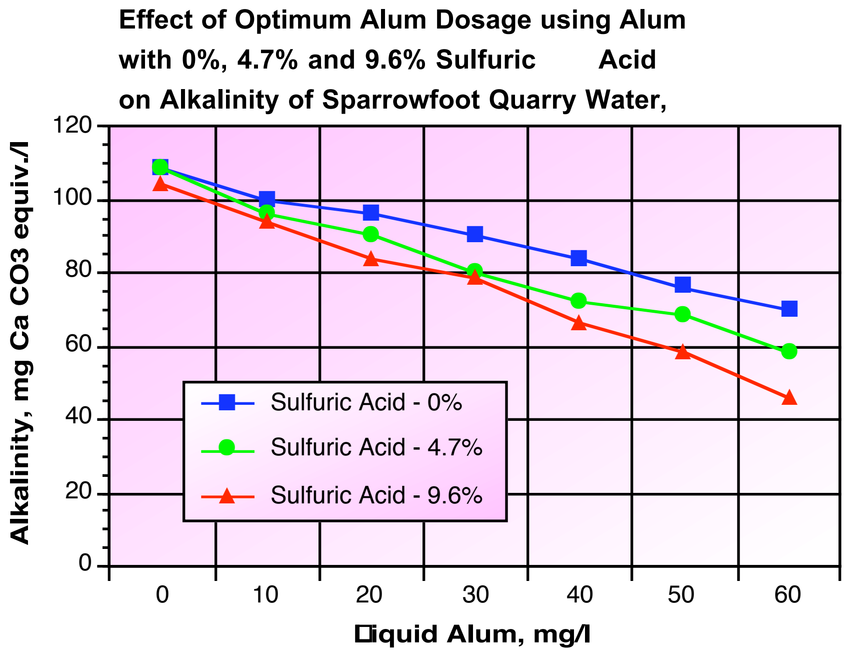


Figure 4.



Effect of Coagulant Addition on Alkalinity of Sparrowfoot Quarry Water

The addition of 'filter' alum alone consumes alkalinity as shown in Figure 4 (Liquid Alum + 0% Sulfuric Acid). Although the consumption of alkalinity is significant at high alum dosages, Sparrowfoot Quarry has sufficient alkalinity to neutralize the acid produced by the hydrolysis of the aluminum ion added.

The addition of sulfuric acid along with the alum further consumes alkalinity. This acid addition is made in an effort to reduce pH levels to those believed by USEPA to 'enhance' removal of dissolved organic matter. For a water with the initial alkalinity of Sparrowfoot Quarry (≈ 110 mg $CaCO_3$ equivalent / l), the "maximum" pH is 6.3 (Guidance Manual for Enhanced Coagulation...USEPA, DWSD, July 1994).

In some of the subsequent studies, an 'alkalinity adjustment' was made after coagulation to restore the original alkalinity of the Sparrowfoot Quarry water. Sodium carbonate (in lieu of lime) was used for this purpose. While lime would be used to adjust alkalinity in the proposed treatment scheme, it does not dissolve completely in short-term studies and would not perform the consistent alkalinity adjustment required in these treatability studies.

II. Determination of Effect of Addition of PAC on Removal of Organic Matter

The second series of studies included a sampling of the Sparrowfoot Quarry water for analysis of initial TOC and TTHMFP prior to treatment. A portion of the Sparrowfoot Quarry water was passed through a neutron track-etched polycarbonate membrane filter with pores of 1.0 µm. This membrane filtration removed particulate matter (silt, clay, bacteria, fibers, organic debris) which would be expected to be enmeshed in alum floc during conventional treatment.

In addition, studies were conducted to assess the effectiveness of conventional treatment in removing organic matter, as indicated by TOC and TTHMFP reductions, using the alum coagulating agents previously evaluated. A description of these coagulants is given in Table 2. The optimum dosage of 40 mg/l of each coagulant was applied during a 45 second rapid mix period. This was followed by flocculation for 25 minutes at 100 rpm and sedimentation for 2 hours.

The treated water was then sampled for TOC and dosed with 8.7 mg chlorine per liter to initiate the 7-day protocol for the measurement of TTHMFP, as per USEPA procedures.

This experimental procedure was repeated with the application of the most acidic coagulant (liquid alum + 9.6% sulfuric acid) and dosages of PAC ranging from 0 to 60 mg/l. The most acidic form of alum was used to lower pH, thereby enhancing the removal of dissolved organic matter. The resulting pH was in the range of 7.1 to 7.3 while the Sparrowfoot Quarry water alkalinity was reduced from 110 mg $CaCO_3$ equivalent / liter to 70 mg/l in each of the alum-coagulated waters.

The results of these coagulation studies, presented in Table 3, indicate that settled water turbidities decreased with increasing PAC dosages. This result is likely due to progressive increases in the specific gravity (normally, 1.01 to 1.10) and settling rate of the alum floc owing to the entrainment of wetted PAC particles (S.G. ≈ 1.3-1.4).

Based on experimental observations indicating a stable, good settling floc plus practical (economic) considerations, a PAC dose of 20 mg/l was selected for the subsequent evaluations of the plant design process.

III. Proposed Plant Process Simulation

The proposed plant process would be best simulated by the use of a pilot plant in which a sludge blanket could be established and maintained. In the present study, efforts were made to adapt bench-scale jar studies to approximate the plant process design.

In all of the simulation tests, 20 mg/l of dry PAC was added to six aliquots of Sparrowfoot Quarry water. The PAC was then mixed for 25 minutes, the theoretical maximum detention time available in the carbon contact basin. The PAC suspension was stirred at a minimum of 100 rpm in order to prevent settling of the heavier PAC particles.

At the end of the 25 minute PAC contact period, 40 mg/l of alum as ‘liquid alum + 9.6% sulfuric acid’ was added to each of six jars. This addition was supplemented by sulfuric acid to yield a pH of 6.3 in the coagulated water. As shown in Figure 5, the addition of the liquid alum reduced the alkalinity to 70 mg CaCO3 equivalent per liter and the supplemental sulfuric acid further reduced the alkalinity to 40 mg/l.

One minute after the addition of alum and adjustment of pH, sodium carbonate was added to restore the initial alkalinity of the Sparrowfoot Quarry water. This increased the final alkalinity to 130 mg/l, as shown in Figure 5 which profiles the changes in alkalinity during treatment.

To simulate the effect of prolonged storage of the alum floc and PAC in the pulsating sludge blanket, the contents of the square beakers used for the jar tests were gently mixed at 40 rpm for periods ranging from 0 to 24 hours.

At the end of each mixing period, the stirring paddles were pulled and the suspension of aluminum hydroxide and PAC were allowed to settle for two hours. Thereafter, samples were taken for TOC and TTHMFP analysis. Again, each sample was dosed with 8.7 mg of chlorine per liter to initiate the TTHMFP. This dosage was selected in an effort to obtain a final chlorine concentration between 1 and 5 mg/l after 7 days of storage prior to analysis for TTHM.

Table 3 presents the results of this test series.

IV. Evaluation of Enhanced Coagulation at Reduced pH for Enhanced Removal of Organic Matter

As an alternative to the plant design process previously evaluated, a study was conducted of the application of alum followed by the addition of PAC. In this series, 40 mg/l of alum as liquid alum plus supplemental sulfuric acid, was applied to reduce pH to 6.3. USEPA has suggested that reducing the pH of water with the initial alkalinity of Sparrowfoot Quarry water to this pH value will result in ‘enhanced coagulation’, increasing the removal of TOC and reducing TTHM forming potential.

Immediately following alum coagulant addition and pH adjustment, 20 mg/l of PAC was applied and long-term (1 - 24 hours) flocculation was initiated to simulate pulsed agitation in an upflow solids contact clarifier. On completion of flocculation, each aliquot was settled for 2 hours prior to sampling for TOC and TTHMFP.

As a control, PAC was not added to one of the test beakers. This was to indicate the degree of removal of organic matter achieved by alum coagulation alone at reduced pH. The results of these studies are shown on Table 4.

V. Evaluation of Removal of Organic Matter without pH adjustment

The final series of studies was undertaken to assess the effectiveness of removal of organic matter if coagulation was not enhanced by lowering the pH to 6.3.

In this series, 20 mg/l of PAC was first applied and mixed for 25 minutes at 80 rpm. Thereafter, 40 mg/l of standard liquid alum solution (0% sulfuric acid) was added along with sufficient sodium carbonate (20 mg $CaCO_3$ equivalent/l) to replace the alkalinity consume (20 mg/l) by the hydrolysis of the aluminum ion. As a result of the simultaneous addition of alum plus sodium carbonate, there was no significant change in alkalinity during treatment.

The coagulated water was then flocculated at 40 rpm for 1 to 16 hours. As in all previous tests, flocculated samples were settled for two hours. Again, no PAC was added to one beaker which served as a control.

The results of this series are presented in Table 5.

Effective turbidity reductions after settling were evident in each of the series of studies. This would indicate that alum coagulation was effective under all test conditions studied.

Summary of Experimental Results

Total Organic Carbon Removals

Sparrowfoot Quarry water was found to contain 6.3 mg C/l (Figure 5). This concentration requires treatment for removal of TOC and indicates that the water is derived from surface water.

Filtration of the quarry water through a 1.0 μm membrane reduced TOC by 21% to 5.0 mg C/l (Fig. 5).

This removal indicates that 21% of the raw water TOC consists of particulate organic carbon which can be removed by particle removal processes, such as coagulation. Activated carbon is expected to remove additional amounts of dissolved organic carbon (DOC).

Alum coagulation is believed to remove a portion of the dissolved organic carbon as well as most of the particulate fraction. Figure 5 shows that 40 mg/l of the three types of liquid alum tested removed an average of 40% of the TOC. The liquid alum with 9.6% sulfuric acid added achieved the greatest (49% removal).

The results of studies to evaluate the incremental removal of TOC by PAC are shown in Figure 6. For the five PAC dosages, the average TOC reduction was 50% as compared to 49% for alum alone. The maximum TOC removal observed was 57%. The results indicate that, even at high dosage, PAC has very limited capability for adsorbing dissolved organic carbon from Sparrowfoot Quarry water.

Figure 5. Total Organic Carbon in Sparrowfoot Quarry Water and after Coagulation with the Optimum Dosage of Alum (+ 0%, 4.7%, 9.6% Sulfuric Acid)

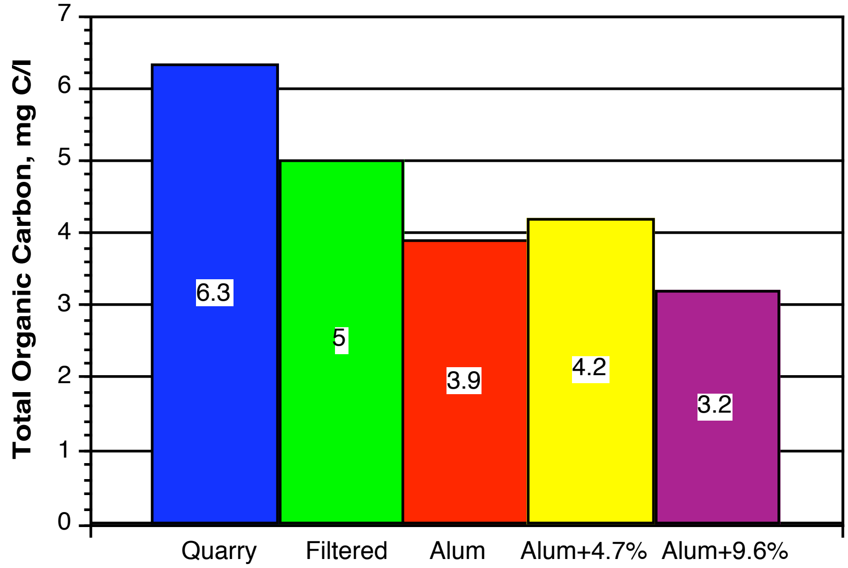
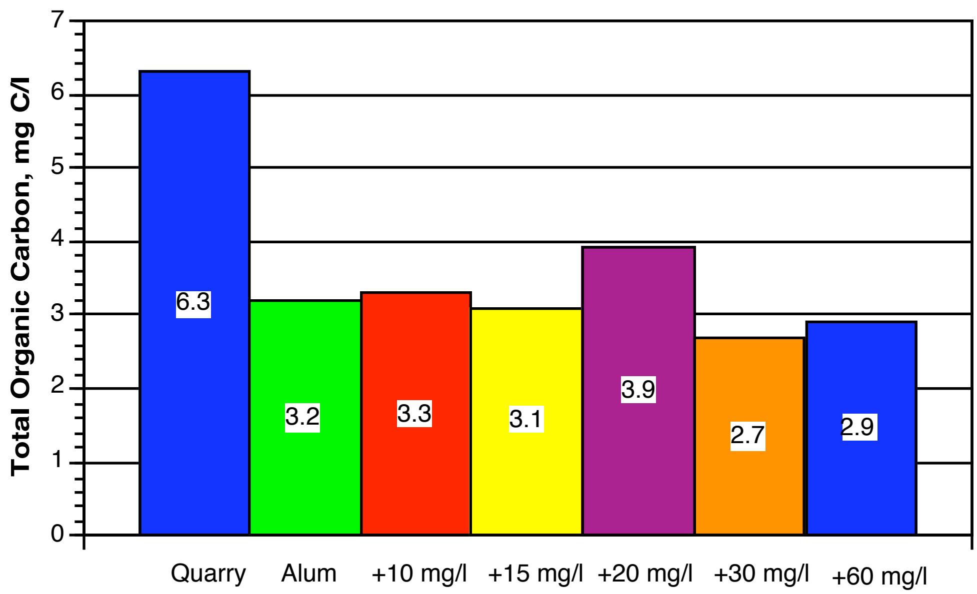


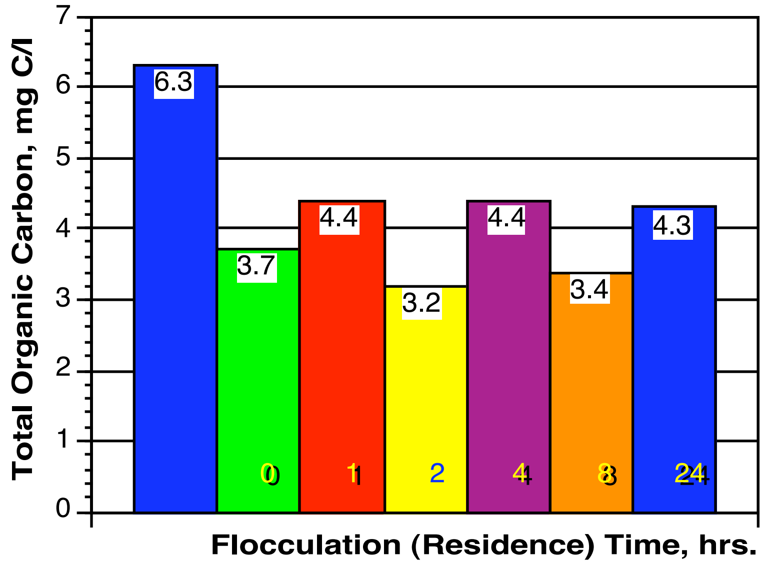
Figure 6. Total Organic Carbon in Sparrowfoot Quarry Water and after Coagulation with 40 mg/l Alum + 9.6% H_2SO_4 following Addition of 0, 10, 15, 20, 30 and 60 mg/l PAC



The process design for the new treatment plant provides for the addition of PAC prior to alum coagulation. The concurrent addition of sulfuric acid lowers pH to values at which DOC is expected to precipitate as particulates (organic colloids) which can subsequently be removed by entrainment in coagulant floc.

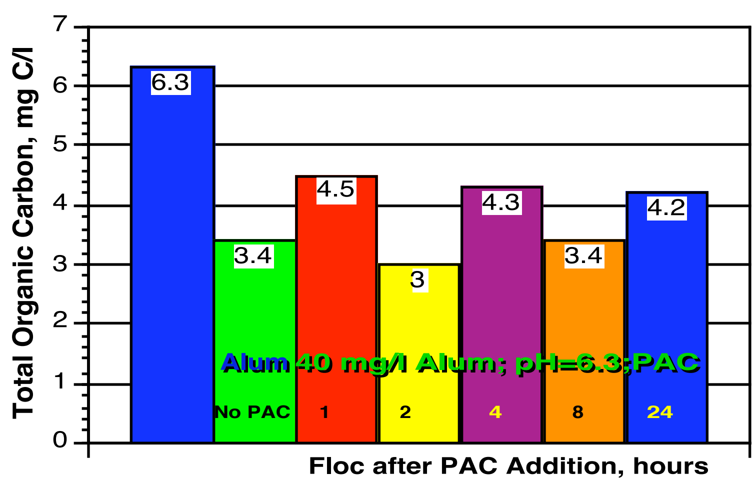
A series of tests simulating the plant process design was conducted. The results, presented in Figure 7, indicate that flocculation periods of up to 24 hours had little effect on TOC removal. Moreover, TOC removals averaged 38%, approximately equal to the removals obtained by alum coagulation alone. Despite the prolonged contact times, these results confirm the minimal removal of TOC by PAC previously observed.

Figure 7. Effect of PAC Contact, pH Adjustment, Alum Coagulation and Alkalinity Adjustment on TOC and 7-Day Chlorine Depletion as a function of Flocculation (Residence) Time



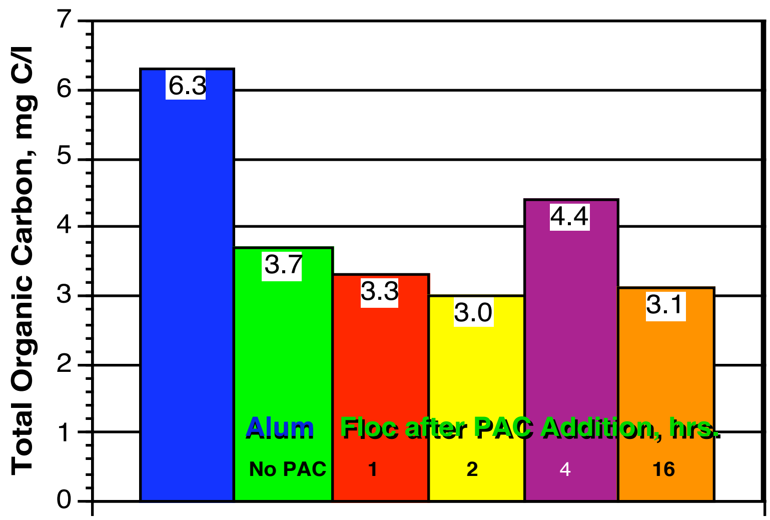
Modification of the treatment protocol to produce an alum floc at pH 6.3, followed by PAC addition, variable flocculation time and sedimentation, resulted in an average 40% TOC removal which was comparable to the process design removals (Figure 8).

Figure 8. Effect of Alum Coagulation, pH Adjustment to 6.3 , PAC Addition, Flocculation for 1 to 24 hours and Final Alkalinity Adjustment on TOC Reduction and 7-Day Chlorine Depletion



Finally, alum coagulation concurrent with PAC and sodium carbonate addition resulted in a 44% removal of TOC, the greatest of the removals observed in the three alternative treatment process test series (Figure 9). Despite the highest pH and alkalinity of the protocols tested, TOC removals were comparable to those observed employing pH control for 'enhanced coagulation'.

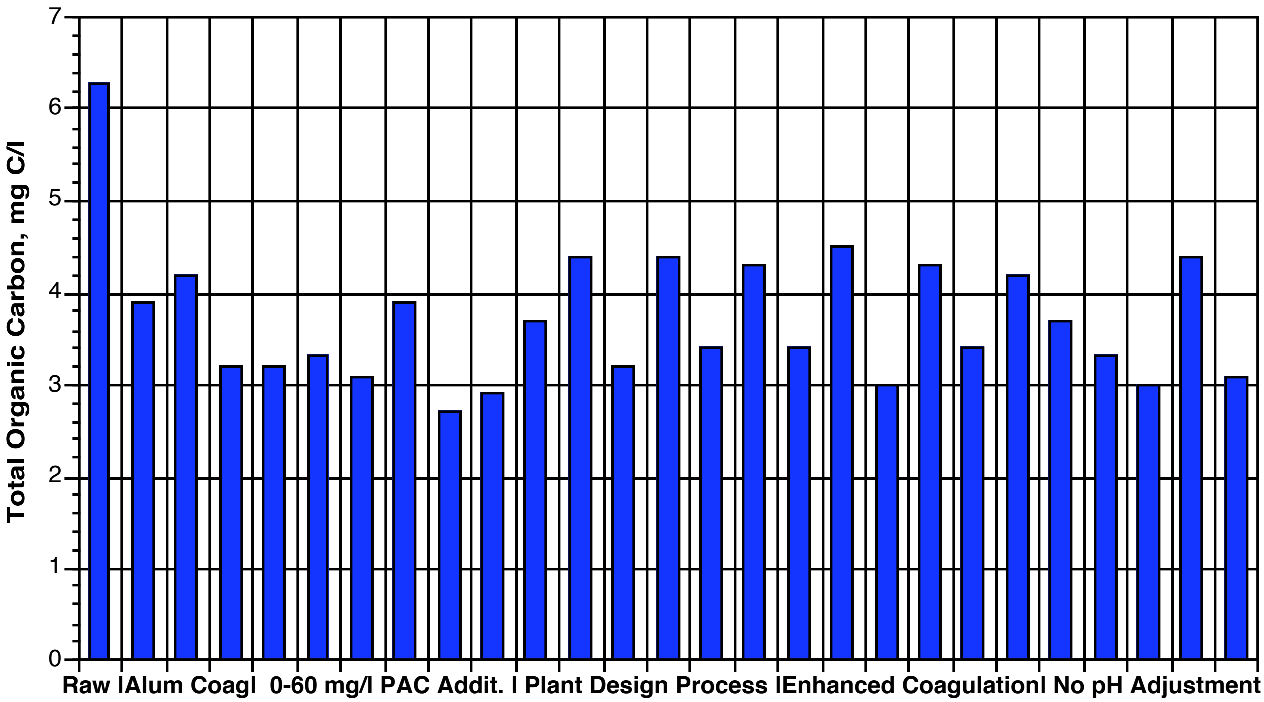
Figure 9. Effect of PAC Contact, Alum Coagulation, Alkalinity Adjustment and Flocculation for 1 to 16 hours on TOC Reduction and 7-Day Chlorine Depletion



In summary, the initial alum coagulation studies averaged 40% TOC removal while the addition of up to 60 mg/l PAC only marginally increased TOC removals to 50%.

TOC removals using the simulated plant design process averaged 38% whereas the modified treatment processes studied averaged 40% and 44% TOC removals, respectively. For all 26 tests conducted, TOC removals averaged 36.2%, with or without PAC additions (Figure 10). These studies also indicate that alum coagulation at any pH is capable of removing approximately 40% of the TOC and that PAC offers little benefit with respect to additional removal of organic matter from Sparrowfoot Quarry water.

Figure 10. TOC of Sparrowfoot Quarry Raw (1) and Alum-Coagulated Waters (2-27)



Finally, a comparison of TOC was made of the Grande River and Sparrowfoot Quarry waters. The results, 5.5 and 5.3 mg C/l, respectively, indicate that both waters are comparable in organic carbon content. Since a 1980 survey of 55 shallow Missouri groundwaters have shown TOC concentrations in well water to average 1.2 mg C/l, Sparrowfoot Quarry water would have to be considered surface water based on organic content. In addition, the quarry water exhibits significant oxygen concentrations which are atypical of groundwater.

Comparison of Bacterial Cell Removals from Sparrowfoot Quarry and South Grande River Waters

Microscopic examination of both the Quarry and River water sources were conducted as part of this study. Raw and treated water samples of each were passed through a 0.2 μm neutron track-etched polycarbonate membrane filter to retain particles larger that 0.2 μm, including bacterial cells. The membranes were then stained with acridine orange, a fluorochrome which stains bacterial DNA and RNA. Under ultraviolet illumination, the DNA and RNA in the cells fluoresce highlighting the cells as well as particles of silt and clay. In addition, algae, diatoms, carbon 'fines', rust particles, calcium carbonate chrystals, oil droplets, organic films and amorphous debris can be visualized, enumerated and photographed using epifluorescence microscopy.

Micrographs of Particles in Source and Finished Waters

The 17 attached micrographs were made by epifluorescent microscopy using a research-grade Zeiss Axiophot microscope.

Sparrowfoot Quarry water is seen to have a large number of very fine clay and silt particles in suspension. Algae and diatoms are evident, confirming the influence of surface water. After treatment at the Public Water Supply District #2 treatment plant, only a few bacterial cells are evident in the finished water.

The South Grande River which serves as the source for the Henry County Company plant at Clinton, exhibits larger silt and clay particles. Some of these particles are colonized by small bacterial cells (green and yellow). The free-floating, micrometer-sized bacteria appear as small dots or short rods in the micrograph. After treatment, a few planktonic bacterial cells are evident along with what appear to be small fragments of alum floc or organic film.

The numbers of bacteria in both raw and finished waters were enumerated and are shown on Figure 12. Comparable numbers of bacterial cells were found in both source waters. Treatment, in each case, was effective in removing an order of magnitude or more of the cells present. The Henry County plant was particularly effective, possibly due to the high alum dosages normally applied at their facility.

Figure 12.

Bacterial Removal from Sparrowfoot Quarry and South Grand River at Clinton, Missouri

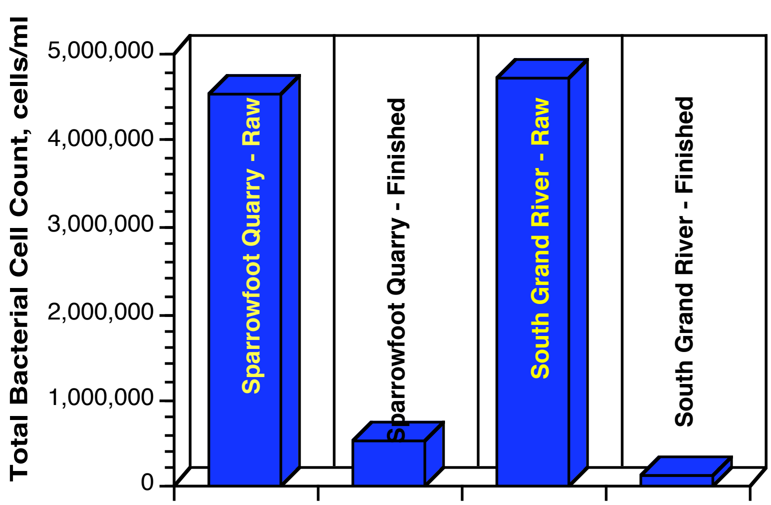


Table 2. Alum Coagulants and Powdered Activated Carbon Evaluated

Aluminum Sulfate	% Al_2O_3	% $Al_2(SO_4)_3$	% $Al_2(SO_4)_3 \cdot 14H_2O$
Standard liquid alum	8.30	27.81	48.31
Liquid Alum + 4.7% sulfuric acid	6.70	22.45	38.99
Liquid Alum +9.6% sulfuric acid	5.40	18.09	31.43

Al_2O_3: 102 a.m.u. $Al_2(SO_4)_3$: 342 a.m.u. $Al_2(SO_4)_3 \cdot 14H_2O$ (Filter Alum): 594 a.m.u.

Ratio of $Al_2(SO_4)_3 \cdot 14H_2O$ (Filter Alum)/ Al_2O_3: 5.82

Continental Chemical Company: Jim Stout 618-271-2430; Chris Lind 1-800-255-7589

Filter Alum Dosages Tested: 10, 20, 30, **40**, 50, 60 mg $Al_2(SO_4)_3 \cdot 14H_2O$/l

Powdered Activated Carbon

Hydrodarco B, steam activated lignite coal: 600 m^2/g, 0.53 g/ml (33 lbs/ft^3) (dry)

Range of PAC dosages evaluated: 0 - 60 mg/l

PAC dosage selected for kinetic studies: **20** mg/l

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