# Particle and Organism Removal Processes at the Kansas City, Missouri Water Treatment Plant

March, 2001

# Process Description

## Source Water Blending

The Kansas City influent water source is, primarily, the Missouri River. Seasonally, the Missouri River supply is supplemented with well water derived from the alluvium of the Missouri River bottoms. Well water is used in the winter to minimize problems due to freezing. Alternately, in the summer, the blending of the river and well waters reduces delivered water temperatures and improves finished water palatability.

## Primary Sedimentation

Primary treatment consists of mixing and sedimentation in six upflow contact clarifier basins. All of the plant settled solid residues (primarily calcium carbonate and magnesium carbonate) are returned to these basins and blended with the plant influent water in their mixing compartments. The return of these lime-precipitated solids aids in influent solids entrainment and sedimentation.

A portion of the returned solids (magnesium hydroxide) redissolves, resulting in the return of magnesium ion ($Mg^{2+}$) to solution. This occurs because magnesium hydroxide solubility increases at the lower pH ($\approx 8.3$) of the blended influent water.

Primary sedimentation at the Kansas City water treatment plant is an efficient, cost-effective means of removing silts, clays, and suspended matter from the turbid Missouri River source. Primary sedimentation also provides up to half of the total removal of microorganisms entering the plant. The six primary sedimentation basins also serve as the central collection point for all of the treatment plant's softening sludge.

The recovery of dissolved magnesium from precipitated softening solids in the primary sedimentation basin is an unusual and highly economic means of recovering an effective coagulant from what would otherwise be a waste material disposed of in a landfill. The practice of coagulant recycling avoids virgin chemical purchase, transportation, storage, additional feed equipment, and modest hazards commonly associated with the handling of inorganic chemical coagulants.

## Chemical Application in Open Channel Flumes

Following sedimentation in the primary basins, water is transported to the secondary basins in six open channels or flumes. The open-channel design makes it convenient to feed, mix and blend a wide range of chemicals. Hydraulic jumps in each flume provide regions of high turbulence that aid in dissolving and dispersing the added chemicals.

Following slaking (hydrating dry lime with water at elevated temperature), a lime slurry is added to the flume in dosages sufficient for excess lime softening. The pH of the water delivered to the secondary settling basin is carefully controlled through lime slurry feed adjustment to ensure that a pH of 11±0.1 is maintained. High pH (high hydroxyl ion concentration) initiates the precipitation of magnesium hydroxide, which them serves as the primary (recycled) coagulant. On occasion, ferric sulfate is added as a supplementary coagulant.

Periodically, powdered activated carbon (PAC) is added at the flume. PAC is added when tastes and odors are detected in the plant finished water. This is normally a seasonal occurrence, coinciding with the spring break-up of ice along stream shores within the Missouri River basin. Under special circumstances, potassium permanganate (an oxidizing agent), or polymeric coagulants may be added to the water as it is transported through the flumes.

While it can be added at numerous points throughout the plant, chlorine is primarily added in the flume. This addition is accompanied by the addition of an ammonium salt to convert the applied chlorine to chloramine. Chloramine is not only more persistent than chlorine alone, this attenuated oxidant is far less likely to react with the organic substances present in the source water. Primarily of natural origin, these organic materials, both particulate and dissolved, may react to form chlorinated organic compounds or disinfection by-products (DBP), such as the trihalomethanes (THM) and haloacetic acids (HAA). Most of the organic precursors to the formation of disinfection by-products are naturally-occuring fulvic and humic substances.

**Secondary Flocculation and Sedimentation**

The six flumes convey the chemically-dosed water to a series of six three-stage paddle flocculators. These units provide gentle agitation for the formation of a large, dense, settleable magnesium hydroxide floc. This floc entrains much of the unsettled particulate matter initially in the source water. This colloidal fraction includes the microorganisms, such as plankton and bacteria.

The flocculators also provide mixing for solution of the added lime, which slowly dissolves and reacts to precipitate calcium carbonate hardness. A portion of the precipitated calcium carbonate is entrained in the magnesium hydroxide floc, increasing the floc density and improving their rate of removal by sedimentation.

The six parallel secondary basins provide extensive surface area for effective sedimentation. Owing to their expanse, the water in the basins is sometimes stirred during periods of high wind velocity. This results in wind-set-up and seiches. However, visual observations of effluent water clarity indicate that, when not hydraulically overloaded, the basins provide good sedimentation efficiency.

Following secondary sedimentation, the magnesium has been precipitated and most of the microorganisms and suspended debris originally in the Missouri River source have been entrained and settled. However, only a marginal reduction in calcium hardness is observed in the secondary effluent. Little more than half of the calcium in the water following the addition of lime (CaO) has been removed. The pH of the secondary basin effluent is maintained at approximately 11.0.

## Recarbonation

The secondary settled water is subsequently conveyed to the recarbonation basins where pH is reduced to about 10.0 by the injection of carbon dioxide ($CO_2$) gas. This treatment establishes the approximate pH of the filtered and delivered water. At pH 10, further magnesium precipitation is arrested and any magnesium hydroxide in carryover floc is solubilized. The dissolution of magnesium hydroxide floc results in a slight increase in magnesium ion concentration in the final basin. However, calcium carbonate precipitation, which is only partially completed during secondary settling, continues.

## Final Sedimentation

Calcium carbonate precipitation, coagulation and clarification occur in the final basins, the third stage of sedimentation at the Kansas city plant. The final basins provide sufficient retention time for roughly half of the calcium ion entering the basin to precipitate and settle. In the absence of magnesium hydroxide as a flocculating agent, the addition of a polymer aids in floc formation, settling and minimization of the quantity of suspended matter which carries over to the filters.

## Filtration

In addition to the precipitated solids carried over from the final settling basin, the filters are confronted with a water that continues to be supersaturated with respect to calcium carbonate. To overcome the tendency of the supersaturated water to form carbonate deposits (scale) on the filter media, a proprietary polyphosphate formulation is added to the final settling basin effluent. The addition of polyphosphate is intended to sequester calcium ion and thereby minimize post-precipitation of calcium carbonate on both filter media and underdrains.

The effectiveness of solids removal and sequestration is evident from operational observations of filter performance. Filter runs are long and effluent turbidities are low, consistently averaging between 0.2 and 0.3 ntu. In terms of overall treatment plant performance, this low filtered water turbidity is particularly significant, considering that much of the residual turbidity (nominally, an indicator of microbial removal efficiency) results from carbonate as well as hydroxide and phosphate precipitates rather than particles initially present in the source water.

**Physical Removal of Particles of Potential Health Significance**

Owing to the mass of precipitated solids formed during treatment, it appears that most of the turbidity observed in the Kansas City filtered and delivered waters is not imparted by those particles of *potential health significance* that were initially present in the influent source water.  In assessing the physical removals provided by water treatment processes, it is the degree of removal of potentially pathogenic organisms from source waters subject to microbial contamination that is of primary concern with respect to public health.

Simple turbidity reductions, which have long been used as a surrogate measures for assessing the degree of removal of pathogens, are not applicable measures of organism removal efficiencies.  This is particularly true where treatment processes generate far greater quantities (mass) of inorganic precipitates than the the mass of influent solids that were initially present in the source water.

A more rational measure of physical removal efficiency would, at least, account for the total solids produced and removed during treatment.  Total solids in the Kansas City treatment process include influent solids plus total calcium carbonate precipitated plus magnesium hydroxide precipitated as the recycled coagulant.  A still more complete accounting would include the iron oxides and additional calcium carbonate formed when the harder well water is blended with the Missouri River water.

Assessments of plant particle removal efficiencies based on overall solids mass removals would confirm what should be intuitively obvious.  Lime softening plants, particularly one with three separate stages of sedimentation, will provide a higher degree of physical removal of particles, including bacteria, virus and protozoans, than most conventional surface water treatment plants employing only one stage of sedimentation.  Owing to the extensive removal by sedimentation, solids removals by filtration is marginal.

## Reductions During Treatment

### Hardness

The hardness of the influent water to the Kansas City plant depends on the blend of well water and Missouri River water. While well water is harder and higher in alkalinity than Missouri River water, it is lower in sulfate ion. Overall, it is similar to Missouri River water in terms of total dissolved solids. On the average, total dissolved solids is reduced by ~30% in the softening process.
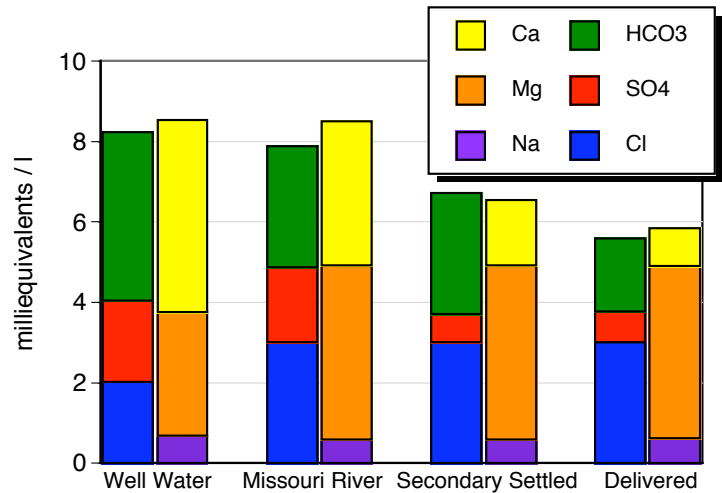


Conversion to milliequivalents per liter allows calculation of cation / anion balance.
meq / l x 50 mg $CaCO_3$ / meq = mg $CaCO_3$ equivalent / l

As the year 2000 bar graphs indicate, on the average, total dissolved solids were reduced by ~30% in the softening process

In addition to dissolved solids, the Missouri River carries a suspended solids load which varies with the flow in the river. Seasonally, suspended solids, mainly silt and clay from soil erosion in the Missouri River basin, are high. With an annual average of 116 mg/l for the year 2000, suspended solids monthly averages varied nearly an order of magnitude from 44 (January) to 426 mg/l (June). Increased suspended solids loads normally increase the required coagulant demands.

The proportion of well water used throughout the year ranges from zero to fifty percent. As a result, the lime dosage required for softening varies with the incoming alkalinity and hardness of the blended water. The higher alkalinity (bicarbonate ion concentration) of the well water is a benefit to the softening process, because more complete softening can be achieved.

Hardness is first reduced in the secondary settling basins following the addition of lime. As previously noted, most of the magnesium ion in the secondary basin influent is precipitated as magnesium hydroxide, while only half of the calcium, including that from the added lime, is removed. As shown in the bar diagram above, there is little net change in the calcium ion concentration in the secondary settled water.

Recarbonation lowers the pH and marginally adds to the carbonate ion concentration. The lowered pH not only prevents further precipitation of magnesium hydroxide, but it redissolves floc which has been carried over from the secondary basin.

Additional hardness reduction occurs in the final basin. The basin provides retention time for the further precipitation and sedimentation of calcium carbonate. While about 40% of the calcium entering the final basin may be removed, magnesium ion appears to increase by 10%, likely due to dissolution of the floc.

Overall, the softening process results in annual average removals, based on Kansas City plant laboratory monitoring data for the year 2000, of 40% of the plant influent calcium and 58% of the influent magnesium ion for a total hardness reduction of just under one-half (46%).

Evaluation of seasonal trends indicated marked differences in calcium and magnesium removals throughout the year. Owing to the influence of temperature on hydroxyl ion concentrations at constant pH, magnesium is considerably more soluble when water temperatures are low (5ºC). In delivered water, magnesium averaged 4.8 mg/l in July and 16.9 mg/l in January.

Whereas magnesium was near constant in the influent from the Missouri River throughout the year, monthly averages of influent calcium varied seasonally. Calcium concentrations varied about 20%, exhibiting higher concentrations in the winter than the summer months.
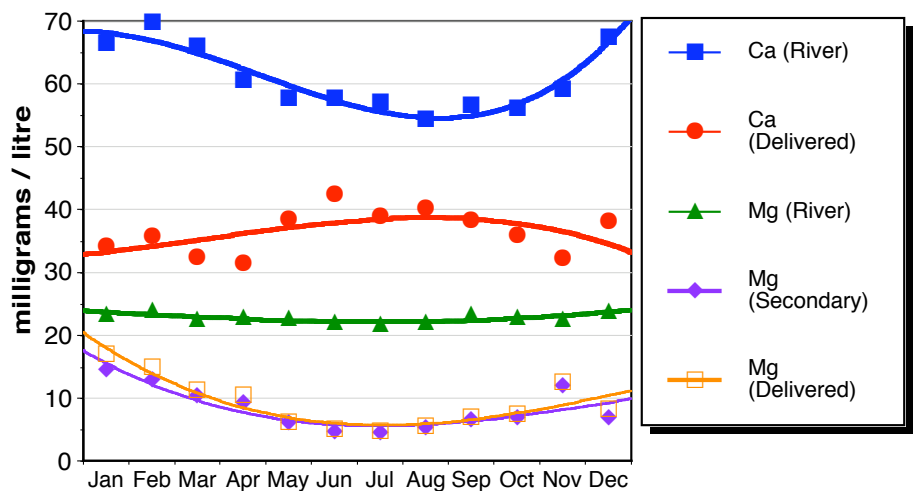


Alternately, monthly average delivered water calcium concentrations were almost a mirror image of the influent concentrations. Monthly averages also varied by approximately 20%, but with the opposite seasonal pattern. As a result of these opposite annual patterns, calcium removal in the year 2000 ranged from a peak of 49% in February to 27% in August.

Seasonal variations in the alkalinity of the Missouri River are similar to those of calcium ion. Both may be influenced by rainfall and reservoir releases.
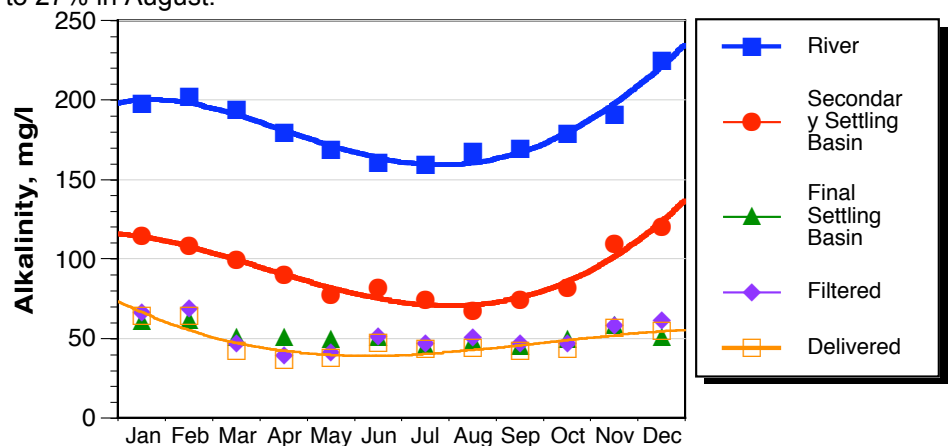
## TOC Removal and Recycling

Examination of Kansas City Water's extensive laboratory database on total organic carbon (TOC) reveals a potential disadvantage in recycling softening sludge to the primary basin influent. As an example, in the month of October 2000, primary basin effluent TOC concentrations occasionally exceeded influent concentrations by as much as 1 mg C/l. The TOC increase through the primary basin averaged 0.48 mg C/l or 12%. Much of this increase may result from the return of particulate organic matter in the recycled softening sludge to the primary basin. The particulate portion of the primary effluent TOC should subsequently be removed in the secondary basin.

As expected, TOC removals in the secondary basins were substantial, averaging almost 2 mg C/l or 44% in October 2000. Further reductions in the final basins and on the filters, if any, were marginal. However, a further 10% reduction in average TOC concentrations was observed following disinfection and storage in the clear well (delivered water). This last reduction may be attributable to the oxidation of organic matter by the disinfectant.
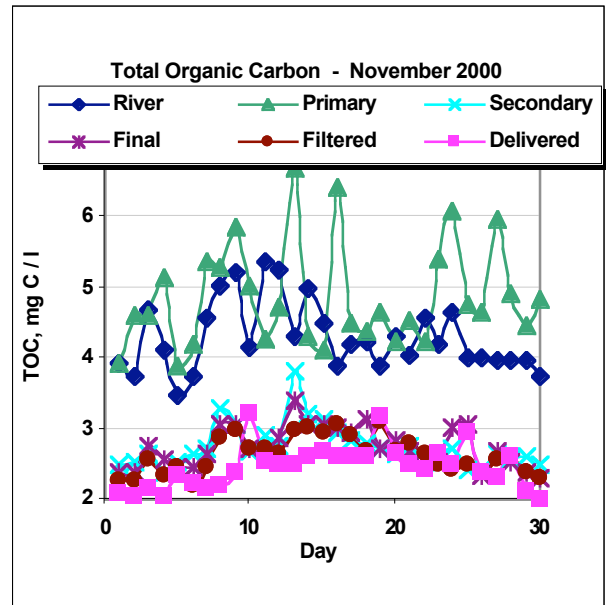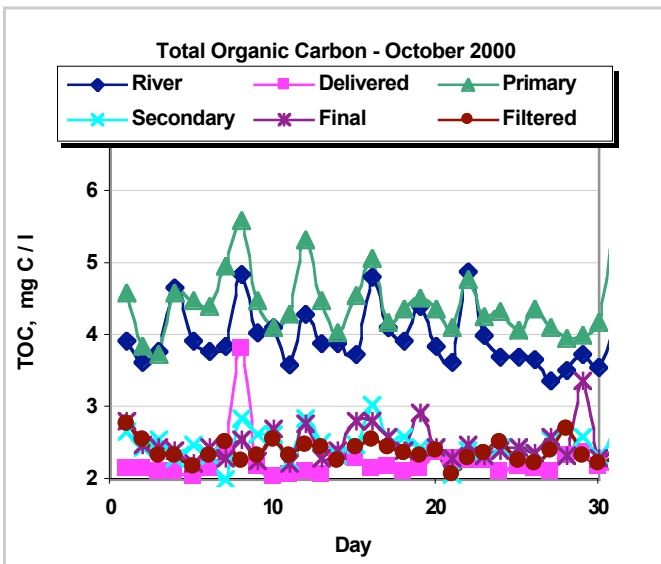
**Turbidity**

Source water turbidity and suspended solids are of special concern to all water utilities, particularly those utilizing surface waters subject to contamination by human and animal wastes.  The physical removal of the particles creating *influent* water turbidity, as opposed to the turbidity incidentally generated by precipitating solids during the treatment process, is of concern owing to a surface water's potential for transmitting pathogenic organisms.

At Kansas City, the quantity of precipitate formed in the lime softening process commonly exceeds the monthly average influent suspended solids.  Monthly average suspended solids in the Missouri River ranged almost an order of magnitude from 44 (January) to 426 mg/l (June) in the year 2000.  Micrographs made as part of the current study indicate that the lime-precipitated solids tend to enmesh and aid in the removal of those solids found in the source water.

As a result of the generation of suspended solids during treatment, source water suspended solids removals and turbidity reductions are both poor indices of particle removal efficiency.  Even so, monthly average turbidity reductions at the Kansas City plant, with its three separate stages of sedimentation, averaged 99.3% and ranged up to 99.95% in 2000.

Turbidity reductions were greatest in June and July when influent suspended solids were greatest (300 to 400 mg/l).
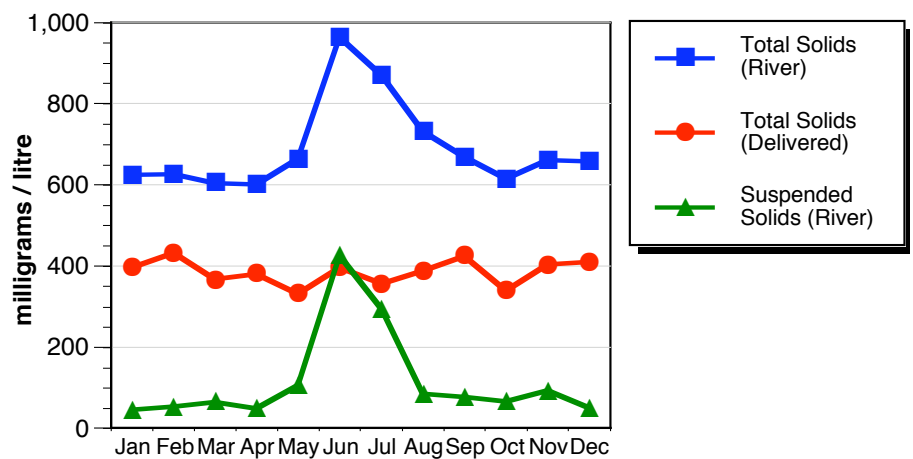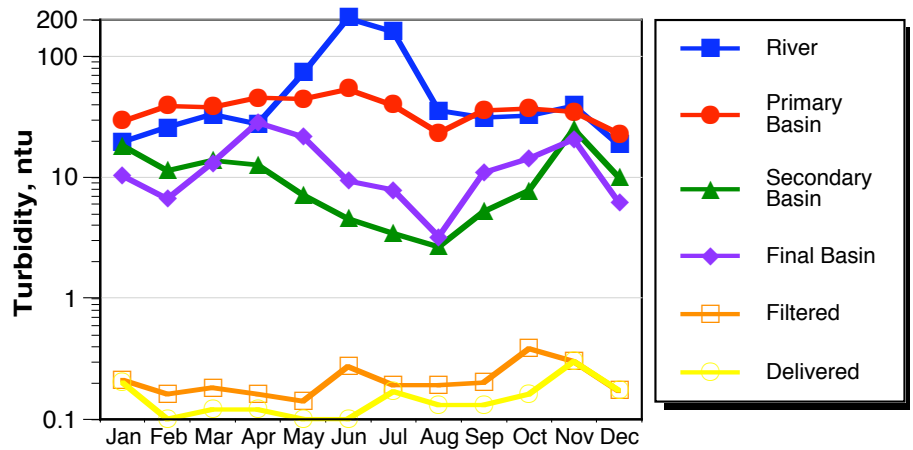
**Coliform**

The microbiological water quality of source and treated waters have long been assessed using the members of the coliform group of organisms, some of which originate in the feces of warm-blooded animals.

Despite enumerating source water monthly averages of 5,000 to 15,000 total coliform organisms per 100 ml during the year 2000, neither total coliforms nor fecal coliform were detected in the delivered water.  In Missouri River water, fecal coliform comprised ~ 5 to 10% of the total coliform population.

As an added safeguard, the Kansas City laboratory monitors fecal streptococcus in the delivered water.  None were detected through the year 2000.
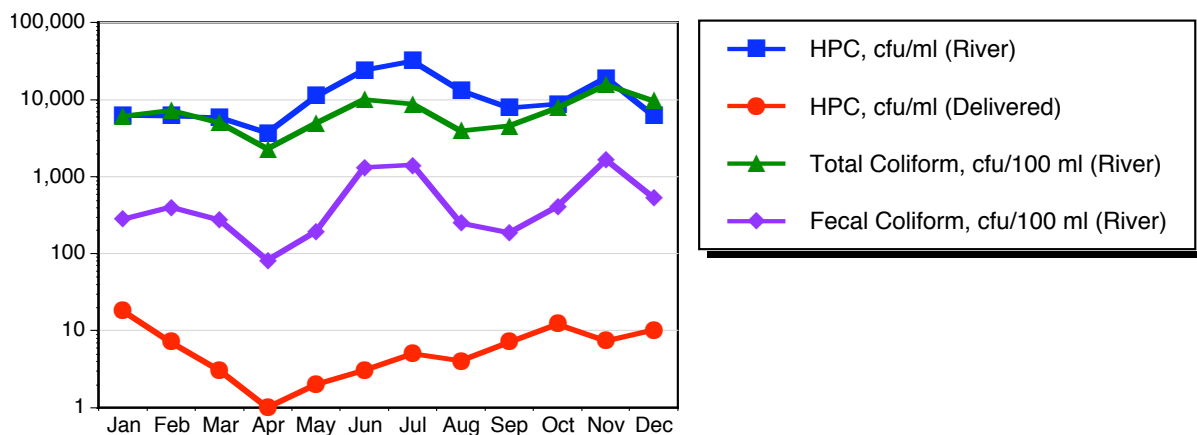


**HPC Removal and Inactivation**

Heterotrophic bacterial plate counts are reduced both by physical particle removal and the loss of organism viability due to the action of the disinfecting agents, chlorine and lime.  The observed 99.995% overall reduction in annual average HPC is therefore greater than that obtained by the physical processes of coagulation, sedimentation and filtration alone.  Even while HPC reductions were not complete, they exceeded the highest observed turbidity reductions by an order of magnitude.

In the year 2000, HPC reductions were lowest (99.7%) in January.

**Removal of Plankton and Actinomycetes**

While most water utilities do not conduct analyses for plankton, their enumeration should be an excellent indication of the efficiency of particle removal processes for the removal of cysts and particle-

associated organisms.  Kansas City data on plankton confirm the effectiveness of primary sedimentation in consistently removing the majority of the microorganisms found in the influent water.  Annual average plankton counts were reduced by over three-quarters (76%) during primary treatment.

Similarly, actinomycetes, a filamentous, branching bacterium associated with earthy/musty tastes and odors, was found to be reduced by 64% during primary treatment.  This would confirm the removal of microorganisms over a broad size range.
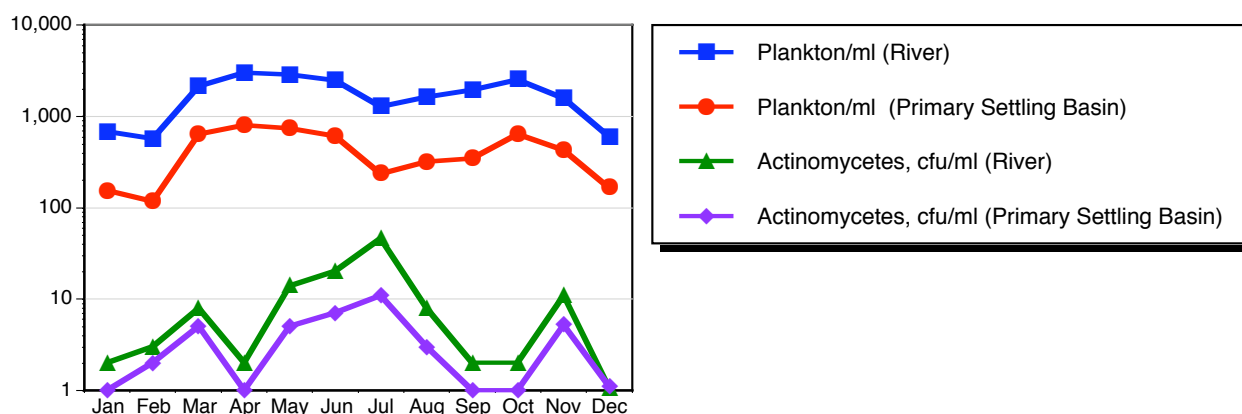


## Direct Microscopic Cell Count

The method used for the enumeration of total bacterial cells in the evaluation of Kansas City water treatment process efficiency was a direct count procedure utilizing neutron track-etched polycarbonate membrane filters and epifluorescence microscopy.  The method was developed and refined by Hobbie et al. in 1977.  After extensive scientific evaluation, it found wide use among microbiologists from the fields of limnology, oceanography, and microbial ecology.  It has been used for the enumeration of microorganisms in food and dairy products (Pettipher and Rodrigues, 1982; Pettipher, 1983; Rodrigues and Pettipher, 1984), intravenous fluids (Denyer and Ward, 1983), urine (Pettipher 1983), ultrapure water systems (Mittelman, et al., 1983, 1985), beverages and wine (Pettipher, 1983; Cootes and Johnson, 1980), and petroleum (Geesey, et al., 1985).  In 1985, it was issued as an ASTM standard method.

In the present plant evaluation, approximately two million (1,990,000) bacterial cells per milliliter were enumerated by direct microscopic cell count in plant influent consisting of 95% Missouri River and 5% well water.  After mixing with return softening sludge, followed by primary sedimentation, this number was reduced to 780,000 cells/ml, a 61% reduction.  This primary sedimentation reduction appears consistent with the observed removal of actinomycetes (64%) and the larger plankton (76%).

Alternately, with limited return sludge, primary sedimentation effluent contained 1,355,000 cells/ml, a 32% reduction.  These results suggest that mixing plant influent with return sludge results in a significant improvement in the removal of bacterial cells by primary sedimentation.

Secondary sedimentation provides further reductions in total bacterial populations. In two separate trials, bacterial cell counts were reduced to 29,500 and 33,500 cells/ml, respectively, following secondary sedimentation. No algal cells were observed microscopically at this stage of treatment, indicating that these larger organisms were more completely eliminated than bacterial cells.

For the two treatment trains studied, lime treatment, flocculation and secondary sedimentation had accomplished further cell reductions of 96% and 97.8%. Starting with Missouri River water, overall cell removals observed after secondary settling averaged 98.4%.

While numbers remained low, an apparent increase in cell counts to 58,000 and 72,000 per ml was observed in the effluents from the final basins. This might be due to sample variation and is within the range of variation of the direct microscopic cell count method.

Two 'delivered' water samples were drawn from the influent and effluent of the plant clearwell. Enumeration yielded 33,500 and 41,000 cells/ml, respectively.

Based on an average of the two clearwell samples, the overall physical removal of bacterial cells during treatment appeared to be 98%.

Direct microscopic observations indicated that most of the remaining microbial cells in the finished water were discolored (faded) and in various stages of decomposition (appearing as 'shadow' or 'ghost' cells). Since this fading was first observed following the addition of lime, it appears that treatment with lime to a pH of 11 may have been partially responsible for the decay (lysing) of the cells not directly removed.
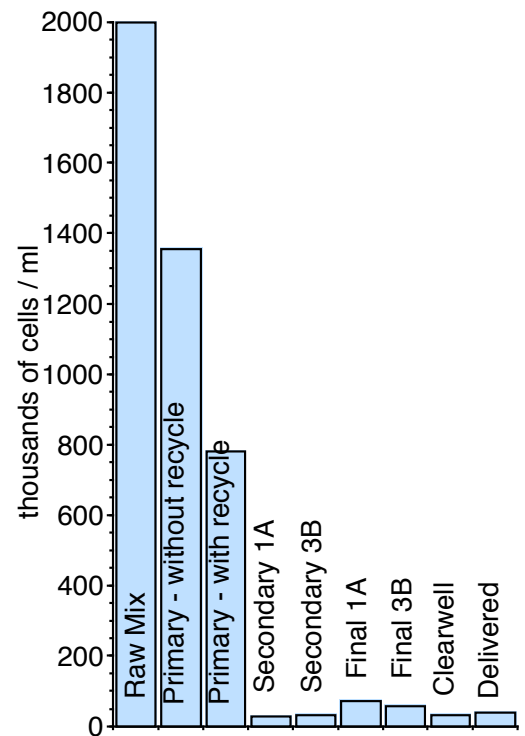
ASTM D4455–85, (1985), Standard Test Method for Enumeration of Aquatic Bacteria by Epifluorescence Microscopy Counting Procedure. *Annual Book of ASTM Standards, Vol. 11.02 Water (II)*, pp. 632–635. ASTM.

Hobbie, J.E., Daley, R.J., and Jasper, S., (1977), "Use of Nuclepore Filters for Counting Bacteria for Fluorescence Microscopy." *Appl. Environ. Microbiol.* 33:1225.

## Seasonal Effects on Source and Treated Water Quality Parameters

*Dissolved Oxygen*

Surface water dissolved oxygen levels are near saturation values throughout the year. The Missouri River water averages 94% of maximum oxygen solubility, while the Kansas City delivered water averages 98% saturation due to the entrainment of oxygen in open basins during treatment. Lower dissolved oxygen concentrations during the summer months are the result of reduced gas solubility at higher temperatures.
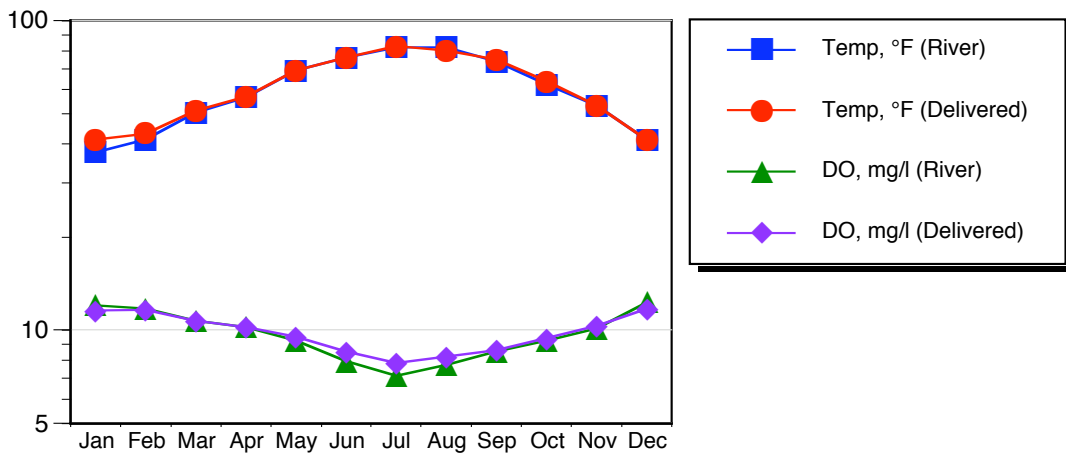


*Temperature*

The effect of the Missouri River on the temperature of Kansas City's supplementary well water supply is evident from the following figure. In the months of August and September, well water temperatures steadily increase until they approach the temperature of the river water itself.
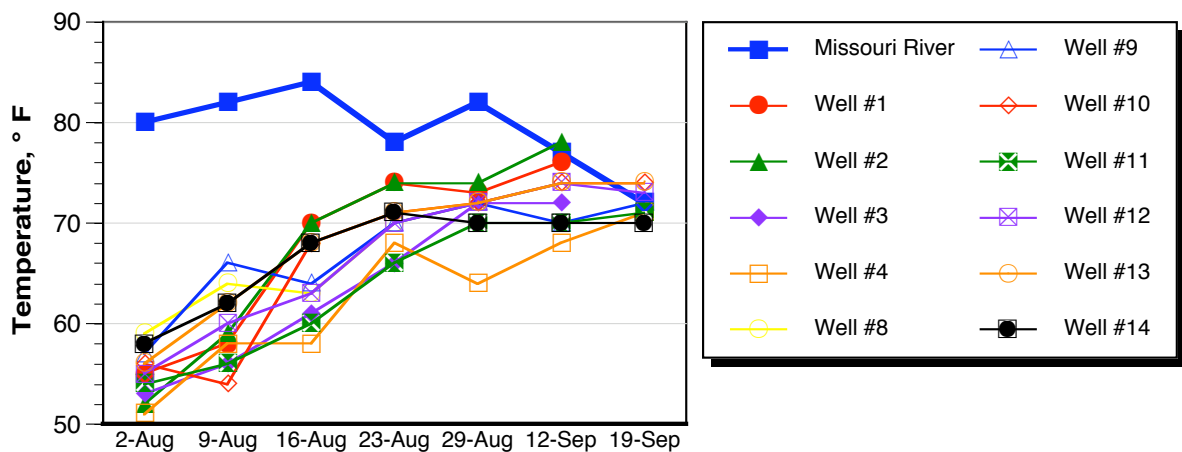
*pH*

In the year 2000, the monthly average Missouri River pH ranged from 7.9 (winter) to 8.4 (summer). Lower River water pH values were recorded in the winter when $CO_2$ solubility is highest   Blending with return sludge in the primary basin increased the pH to between 9.1 and 9.5.  The subsequent addition of lime in the softening process was adjusted to maintain a near-constant pH of 11 in the secondary settling basins.  Finally, adjustment of pH to ~ 10 by recarbonation established the pH in the final settling basins, filter effluents and clear wells (delivered water).
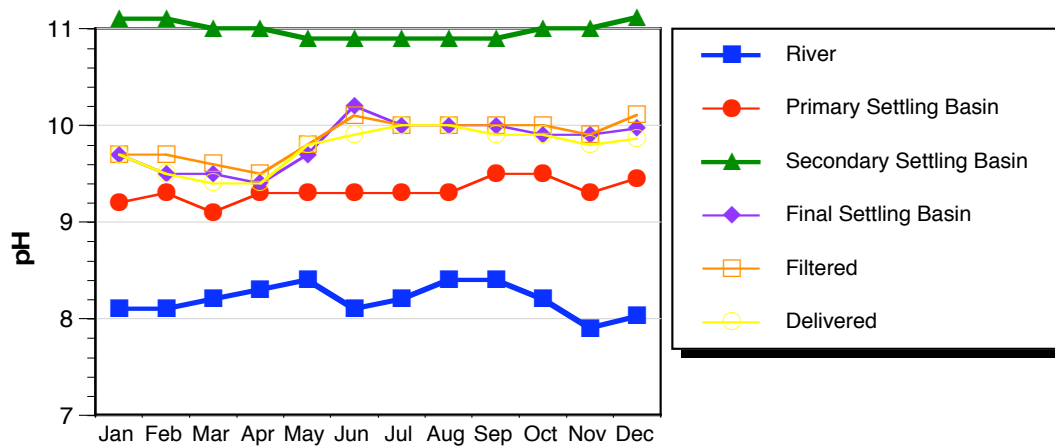


*Nitrogen*

The monthly average concentration of nitrate ($NO_3^-$) ion in the Missouri River varies significantly throughout the year (0.1-1.5 mg N/l), presumably as a result of agricultural practices.  Data from the year 2000 indicates an average of 11% removal of nitrate in the treatment process.

Ammonium ion in the Missouri River water is consistently low throughout the year.  The increase in the delivered water results from ammonia added within the plant in order to form chloramines.  The chart at right suggests that the ammonia feed may have been reduced in the summer in an effort to reduce excess ammonium ion leaving the plant.

In general, the ammonia feed should be carefully controlled to ensure that no free chlorine remains while minimizing the free ammonium ion.
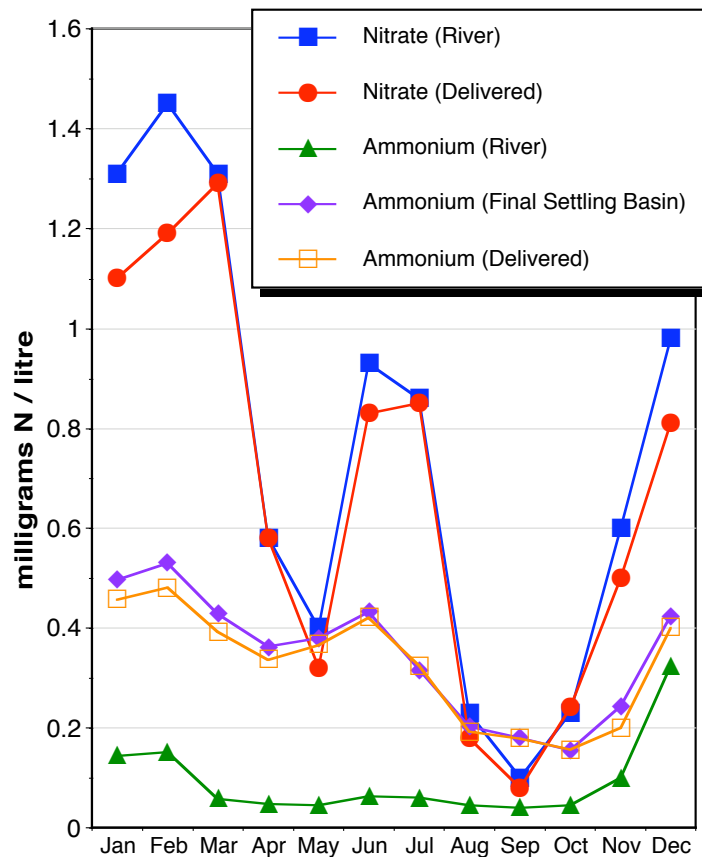
**Magnesium as a Recycled Coagulant**

In the absence of supplemental coagulant additions, the concentration of magnesium ion ($Mg^{2+}$, not total magnesium) in the effluent from the primary basin is critical to the subsequent coagulation, flocculation, and sedimentation of the lime-treated water in the secondary basin.  Data for the year 2000 shows that magnesium in the primary basin effluents varied seasonally.  The lowest concentrations were observed in the summer months.
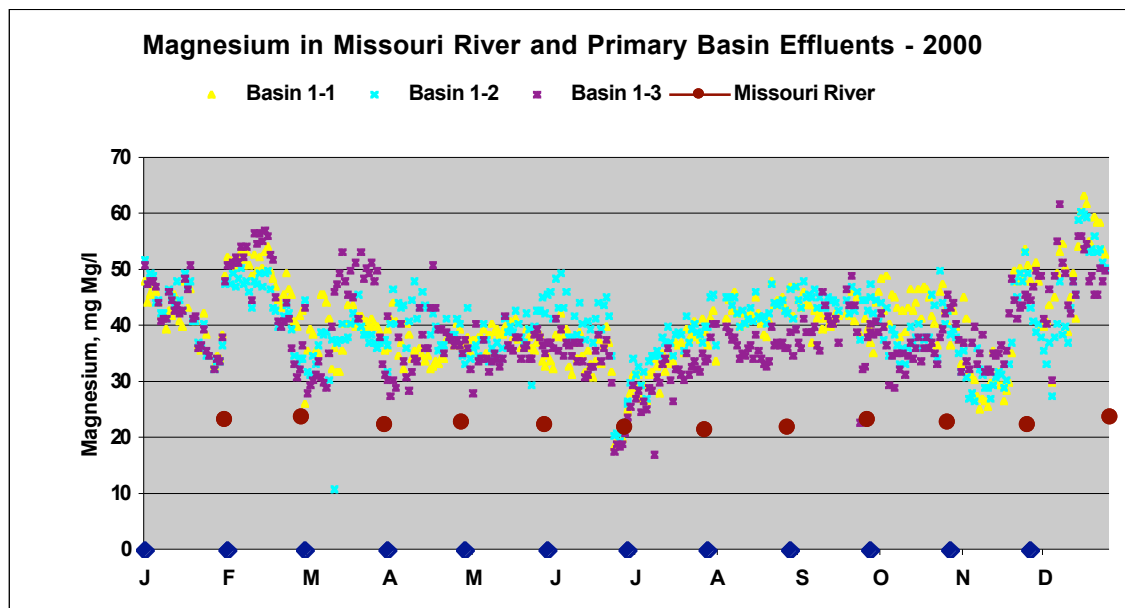


The amount of magnesium recovered as a recycled coagulant can be calculated as the difference between the primary basin influent and effluent concentrations.  The Missouri River, which constitutes most of the primary basin influent, averaged 22.7 mg $Mg^{2+}$/l in the year 2000, whereas the primary basin effluent averaged 39.8 mg $Mg^{2+}$/l.  Before accounting for the contribution of the well water, it appears that the average magnesium concentration increase was 17.1 mg $Mg^{2+}$/l.

Analytical data for magnesium ion in the well waters, however, indicate that the blending of the river and well water has little effect on the primary basin influent magnesium ion concentration.  The well waters averaged 23.7 mg $Mg^{2+}$/l as opposed to 22.7 mg $Mg^{2+}$/l for the Missouri River.

With daily variations in the return rates of recycled softening sludge, the increase in magnesium ion may be, at times, marginal or insufficient for effective coagulation.

Several determinations should prove useful for future plant operation with respect to coagulation and residuals management:

- Magnesium dose-response curves for the coagulation of lime-treated primary basin effluent, performed over a range of temperatures, should be developed to bracket the $Mg^{2+}$ concentrations that provide optimum particle entrainment, settling rates, and clarification.

- Operational methods that facilitate the monitoring and control of magnesium ion following solids recycling in each of the six primary basins should be codified so that, where magnesium concentrations are found to be inadequate, modified recycle or mixing protocols can be implemented.

- Studies should be conducted to determine the feasibility of utilizing an alternate or supplementary procedure for recovering magnesium ion from the softening residues.  Batch treatment of sludge with carbon dioxide should return high concentrations of magnesium to solution.  This concentrated supernatant might then be returned to the primary basins to augment the magnesium derived from direct solids recycling.

- To further assess the feasibility of recovering additional magnesium ion, the magnitude of return of organic carbon should be determined as a function of the concentration of magnesium ion recovered.

**Effect of Solids Recycle**

Presently, solids recycle occurs solely in the mixing zone of the primary clarifiers.  Different solids concentrations may be obtained depending upon softening sludge density, primary influent flow, and solids recycle rates.  At one time in the past, however, a portion of the recycled solids were returned to the flume along with the lime feed.

To evaluate the influence of returning solids to the flume, jar test studies were conducted with added dosages of return sludge ranging from 0 to 40 mg/l.  No improvement in the rates of coagulation or sedimentation was observed.  Instead, as shown in the photographs below, the turbidity of each settled water sample increased with the dosage of return solids.

The observed turbidity increase was due to the added suspension of calcium carbonate and magnesium hydroxide.  This suspension did not aid in the coagulation of the lime-treated primary effluent.  These results would indicate that, if return solids are added after the addition of lime, magnesium hydroxide will not have as great an opportunity to return to solution as it would have at the lower pH of the primary influent.  In the supernatants from the six trials, illustrated below, magnesium ion ranged from 7 to 9 mg Mg/l and calcium ion from 42 to 52 mg Ca/l.  These results support the decision of Kansas City Water to discontinue the return of softening sludge to the flume.

**Coagulation with Recycled Magnesium plus Ferric Ion**

An evaluation of the coagulation of lime-treated primary basin effluent was conducted, because it appeared that, as influent water temperatures declined with the onset of winter, secondary settling tank effluent increased in cloudiness, and floc could be seen passing over the effluent weirs.

The initial coagulation tests utilized *primary settled water* following the addition of lime. The pH of the lime-treated water varied only slightly around 11. In addition to the recycled magnesium ion, ferric sulfate was added to provide ferric ion as a coagulant aid. At the elevated pH, both magnesium and ferric hydroxides readily precipitate to form white and orange floc, respectively.
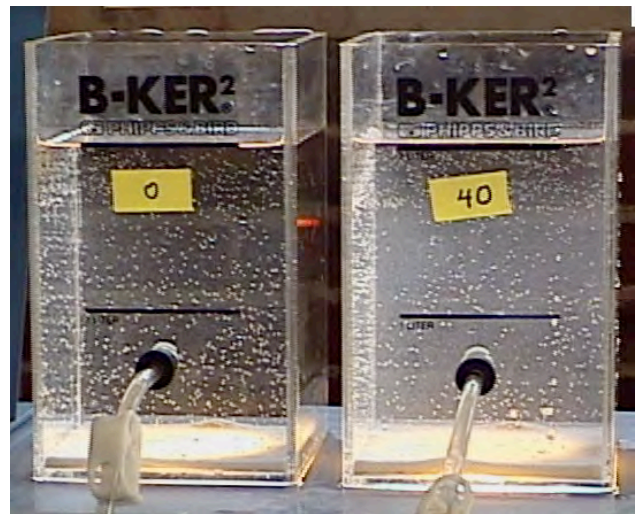


The results of the first jar tests indicated that magnesium hydroxide precipitation alone provided an acceptable degree of coagulation and settling. However, as in the secondary settling basin itself, there was evidence that a portion of the microfloc in the jar test suspension did not settle readily. The test water temperature was between 6 and 7°C.

The addition of 10, 20 and 30 mg/l of ferric sulfate resulted in progressively improved coagulation, floc settling, and supernatant clarification. Combined with the magnesium hydroxide precipitate, each of the supplemental iron dosages resulted in a well-clarified supernatant.

These results indicate that the elevation of the concentration of magnesium ion resulting from the return of softening sludge may have diminished with decreased water temperature. Magnesium ion, 23 mg/l in the primary basin influent, increased by only 6 mg/l following the return, mixing and resettling of the recycled sludge. This marginal recovery of magnesium ion appears to be insufficient to yield an effective coagulant dose.

Even the subsequent addition of lime to raise the pH to 11 failed to result in significant precipitation of magnesium hydroxide. The lime-treated primary basin effluent increased in cloudiness as the result of calcium carbonate precipitation, while only 6 mg Mg/l appears to have precipitated. After prolonged settling, the supernatant remained turbid and the settled material appeared largely granular.

Ferric sulfate [$Fe_2(SO_4)_3$] was added as a supplemental coagulant in an attempt to improve supernatant clarity. Each of the three trial dosages (10, 20, 30 mg Fe/l) resulted in a clear supernatant. However, the acid produced by the hydrolysis of ferric ion in precipitating ferric hydroxide increased calcium carbonate solubility marginally and increased the concentration of calcium ion in the supernatant. As the data indicate, the greater the ferric sulfate dosage, the harder the settled water. These results confirm the decision of Kansas City water to discontinue or limit the supplemental feed of an acid-producing, inorganic coagulant.

The following photographs illustrate the comparative clarification of *lime-treated primary settling basin effluent* by magnesium ion alone and in combination with ferric ion.

| Primary Basin Influent (Control) | Primary Basin Effluent (after sludge return & settling) | Primary Basin Effluent + Lime (pH 11) | Primary Basin Effluent + Lime + 10 mg/l Fe | Primary Basin Effluent + Lime + 20 mg/l Fe | Primary Basin Effluent + Lime + 30 mg/l Fe |
|---|---|---|---|---|---|
| 62 mg Ca/ l 23 mg Mg/l | 49 mg Ca/ l 29 mg Mg/l | 17 mg Ca/ l 23 mg Mg/l | 26 mg Ca/ l 23 mg Mg/l | 30 mg Ca/ l 25 mg Mg/l | 40 mg Ca/ l 26 mg Mg/l |
| 249 mgCaCO3/l | 242 mg CaCO3/l | 136 mg CaCO3/l | 158 mg CaCO3/l | 177 mg CaCO3/l | 199 mg CaCO3/l |
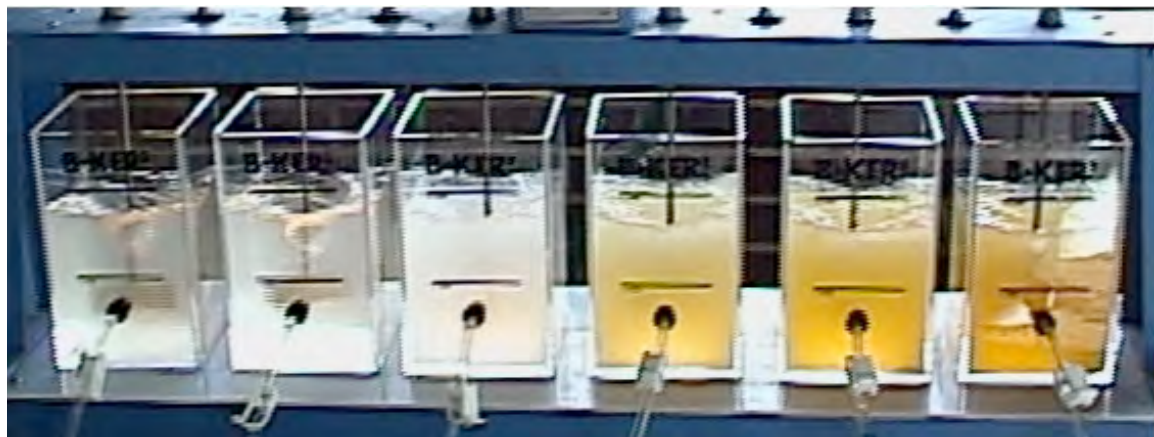
The carryover of magnesium hydroxide floc from the secondary basins in the Kansas City treatment process should have limited effect on filter influent turbidity since the secondary settled water is recarbonated and again settled in the final settling basins. Magnesium hydroxide that escapes the secondary basins may be expected to redissolve at the reduced pH created during recarbonation. This dissolution would increase the magnesium ion concentration and, thereby, the total hardness of the delivered water. Alternately, the final settling basins provide additional time for precipitation of calcium carbonate resulting in a net decrease in final settled water hardness.

## Magnesium Ion Solubility

For the year 2000, magnesium in the Kansas City influent water averaged approximately 23 mg Mg per liter (1 mM or 2 meq/l) . The delivered water averaged 10 mg Mg per liter (0.8 meq/l). From these averages, it appears that, without the return of solids containing magnesium hydroxide, only 23 - 10 = 13 mg Mg/l would have been precipitated to serve as a coagulating agent for the influent suspended solids.

This quantity of magnesium hydroxide precipitate would have been insufficient to serve as an effective coagulant. Instead, the recycle of precipitated magnesium hydroxide to the primary basin influent increased the concentrations of magnesium ion in the primary basin effluent and made it possible to maintain effective coagulation dosages in the secondary basins.

An approximation of the solubility of magnesium ion in equilibrium with magnesium hydroxide (brucite) as a function of pH and at a temperature of 25°C is illustrated on the graph at right.



Mg(OH)$_2$ Solubility

Mg Influent (avg)=23 mg /l

Mg (pH 11 @ 25 C) = 0.24 mg /l

log [Mg2+]

pH
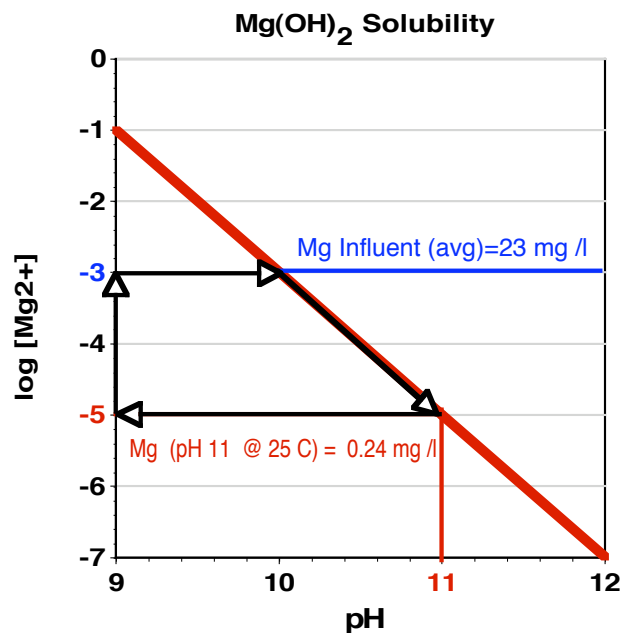
At the pH of the Missouri River, below pH 9, magnesium hydroxide solubility would exceed 2,400 mg Mg/l (100 mM/l). As a result, with favorable magnesium hydroxide solution kinetics and adequate mixing time, a large proportion of the magnesium hydroxide returned to the primary basins should redissolve to increase the magnesium ion concentrations far beyond that present (23 mg Mg/l) in the influent water.

At 25 °C, the subsequent addition of lime to raise pH to 11 reduces magnesium solubility to about 0.24 mg Mg/l if solubility equilibrium is attained. Under favorable conditions, most of the dissolved magnesium ion will be precipitated and recovered as part of the softening sludge in the secondary settling basins.

However, when influent water temperatures decline to 5°C, magnesium hydroxide solubility increases significantly if pH is held at 11. This is partly due to the fact that the ion product of water, $K_w$, decreases significantly with temperature. The following plot illustrates the effect of temperature on the pH required to maintain a constant hydroxyl ion concentration of 1 mM/l (pOH = 3). The figure indicates that, to maintain a pOH of 3, sufficient lime must be added to raise the pH to 11.0 at 25°C and to approximately 11.7 at 5°C. If the pH is not increased, the influence of low temperature on the hydroxyl ion concentration would theoretically increase magnesium solubility by a factor of about 29.





pK Mg(OH)2 versus Temperature
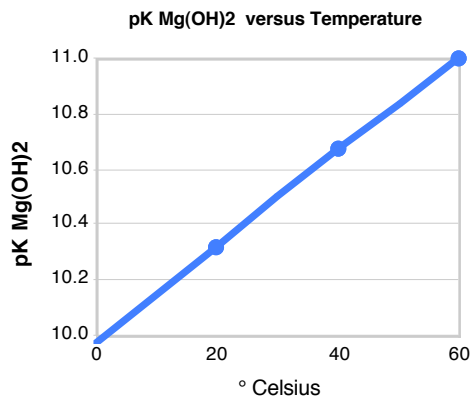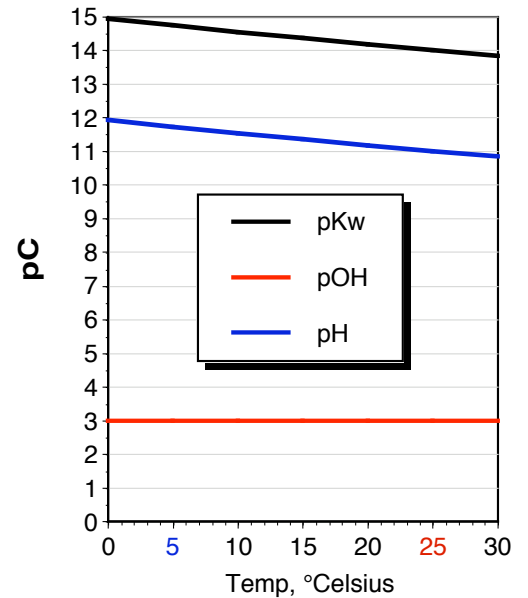
While other equilibria are involved, it is clear that additional lime dosages and higher pH reactions are required to maintain equivalent magnesium softening and coagulation efficiency under cold water conditions.

**Conclusions and Recommendations**

Jar test studies indicate that the return of softening solids to the chemical feed flumes does not have a beneficial effect on the subsequent removal of solids from the lime-treated water. Instead, after the return of solids to the lime-treated primary effluent, coagulation results in increased supernatant water turbidity.

The supplemental addition of ferric sulfate as a coagulant improves the rate of settling and degree of clarification of lime-treated primary effluent. However, since ferric sulfate is a strong acid, the hardness of the supernatant was found to increase with the coagulant dosage over a range of 10 to 30 mg/l. These results confirm the decision of Kansas City to discontinue the use of ferric sulfate as a supplementary coagulant.

Studies were not conducted using polymers as supplemental coagulants. However, properly selected and controlled, appropriate polymers have the potential for strengthening floc, improving settling rates, increasing settled solids density, and altering the characteristics of the settled solids with respect to resuspension and removal (e.g., viscous properties). Kansas City's use of polymers as a supplemental coagulant also avoids the addition of acid. Future, detailed studies should be conducted at various temperatures and magnesium ion (primary coagulant) concentrations to develop a timing and dosage protocol for the use of specific polymers.

Currently, the density of the returned softening sludge is considered low, so that additional sludge pumping is required and primary basin sludge blankets are thin or unstable. Future process evaluations should evaluate precipitated solids density and fluid characteristics to determine whether significant improvements can be obtained using alternative coagulation protocols.

As previously noted, several determinations with respect to magnesium ion recovery efficiency should prove useful for future plant operation with respect to both coagulation and residuals management:

- Magnesium dose-response curves for the coagulation of lime-treated primary basin effluent, performed over a range of temperatures, should be developed to bracket the $Mg^{2+}$ concentrations that provide optimum particle entrainment, settling rates, and clarification.

- Operational methods that facilitate the monitoring and control of magnesium ion following solids recycling in each of the six primary basins should be codified so that, where magnesium concentrations are found to be inadequate, modified recycle or mixing protocols may be implemented.

- Studies should be conducted to determine the feasibility of utilizing an alternate or supplementary procedure for recovering magnesium ion concentrate from the softening residues. Batch treatment of sludge with carbon dioxide or inorganic acid should return high concentrations of magnesium to solution. As required, this concentrated supernatant might then be returned to the primary basins to augment the magnesium derived from direct solids recycling.

- To further assess the feasibility of recovering magnesium ion concentrate, the magnitude of return of organic carbon should be determined as a function of the concentration of magnesium ion recovered.