

**2015 NJ AWWA Annual Conference**  
**Session G – Groundwater**

**Enhancement of Radium 226/228 Removal with HMO**

Erik K. Biermann, P.E., C.M.E., Raymond Jones, Daniel Urban

**Abstract**

The Paulsboro Water Treatment Plant came online in June 2012. The raw water quality from the two new wells made treatment challenging; each had low pH and required treatment for iron, manganese, aluminum, radium and benzene. The treatment processes were designed using pilot and bench scale testing data, however radium removal proved to be the most challenging. A combination of raw water quality analysis and pilot testing indicated that there was enough naturally occurring manganese to implement a radium removal process using the hydrous manganese oxide (HMO) process where radium co-precipitates along with the HMO floc. The HMO process appeared to be quite effective as measured during the intensive testing at start-up (approximate removal was 75 – 85%). However, subsequent quarterly testing showed that the process had become less effective and was then only removing about 30% of the radium. Operations were adjusted in an attempt to improve coagulation, floc formation, and settling. However, the effectiveness continued declining until a year later the 5 pCi/L running average had been exceeded by 0.184 pCi/L. At that point plant operations ceased temporarily. Several conjectures were made regarding the decrease in radium removal efficiency. However, investigations of the current raw water quality and the filter media condition pointed toward the possibility that the HMO created from the naturally occurring manganese was either insufficient for the observed radium concentrations or that other positively charged inorganic metal ions were in competition with radium for adsorption sites on the HMO floc. From the several potential solutions available, Paulsboro chose to implement a new chemical feed system of preformed HMO generated using potassium permanganate and manganese sulfate. With the new HMO feed operating at a rate of 1 ppm, the radium removal is back up to 75 to 85% and finished water concentrations are consistently around 2 pCi/L.

**Introduction & Summary**

The Borough of Paulsboro is located in the western portion of Gloucester County and is bounded by the Delaware River and Mantua Creek. As determined by the New Jersey Department of Environmental Protection, the Borough is at the edge of the area entitled “Critical Area No. 2”, but outside of the depleted zone. The Borough provides water through its three existing wells, Nos. 7, 8 & 9. Water from Well No. 7 is treated at its own water treatment plant with a zeolite ion exchange process followed by pH adjustment via lime addition and disinfection via sodium hypochlorite addition. The water from Well Nos. 8 & 9 is treated at a single treatment plant that takes water from both wells and treats it using GreensandPlus pressure filters as the primary treatment method. All three wells draw water from the Potomac Raritan Magothy (PRM) aquifer system.

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The Paulsboro Water Treatment Plant for Well Nos. 8 & 9 was constructed in 2011 and 2012 and replaced two of Paulsboro's oldest wells and their associated water treatment facilities. Well Nos. 8 & 9 have similar water quality to each other. Both are screened in the same stratum of the middle PRM and the raw water is indicated by its low pH and presence of iron, manganese, aluminum, and radium above the NJ state water quality standards. Benzene was also present in each well at concentrations just below the state standard of 1 ppb. The new plant was brought online in June 2012.

**Description of the Existing Water Treatment Plant and its Operations**

The Paulsboro Water Treatment Plant is designed to treat the water from Well Nos. 8 & 9, where each of the wells has a capacity of 750 gpm for a total flow of 1,500 gpm. The processes were designed to raise the pH and remove iron, manganese, aluminum, radium, and benzene. The plant was constructed with the successive unit processes in two parallel trains. The unit processes in the existing treatment plant are as follows (presented in order):

- Air Strippers: to remove the benzene and introduce oxygen to enhance oxidation and reduce chlorine usage,
- Flash mixers: to introduce chlorine (sodium hypochlorite) to oxidize iron and manganese, and lime to raise the pH,
- Contact tanks: for reaction time and to allow initial formation of the floc,
- Settling basin: for removal of the iron floc to minimize the filter loading, increase the length of filter runs between backwashes, and minimize the fluctuations in water quality,
- Tube settlers: at the discharge of the clarifier to enhance removal of iron floc,
- High service pumps: to provide the flow and pressure required to send the water through the remainder of the treatment plant and out into the distribution system.
- GreensandPlus filters: to remove the remaining iron, aluminum, manganese, and to co-precipitate the radium,
- Post-lime and chlorine (sodium hypochlorite) addition to adjust pH and chlorine residual
- Chlorine contact tank: for disinfection time.

In addition to the main process units, there is a 120,000 gallon backwash tank where the iron and manganese floc that accumulated on the filters during the previous treatment cycle can settle and concentrate. The supernatant is then pumped back into plant just upstream of the GreensandPlus filters. The concentrated iron sludge (i.e. red water) is then discharged to a 35,000 gallon sludge holding tank. The waste is then pumped to the sanitary sewer at a rate of approximately 26 to 38 gpm, where the lower flow rate reduces the disturbance to the sanitary sewer collection and treatment systems.

The treatment plant is controlled by a central SCADA system that receives process data inputs (water levels, flow rates, pH, free chlorine, valve positions, pump status, etc.) and then

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makes adjustments to the well pumps, high service pumps, chemical feed rates and valve positions.

**Initial Plant Operations**

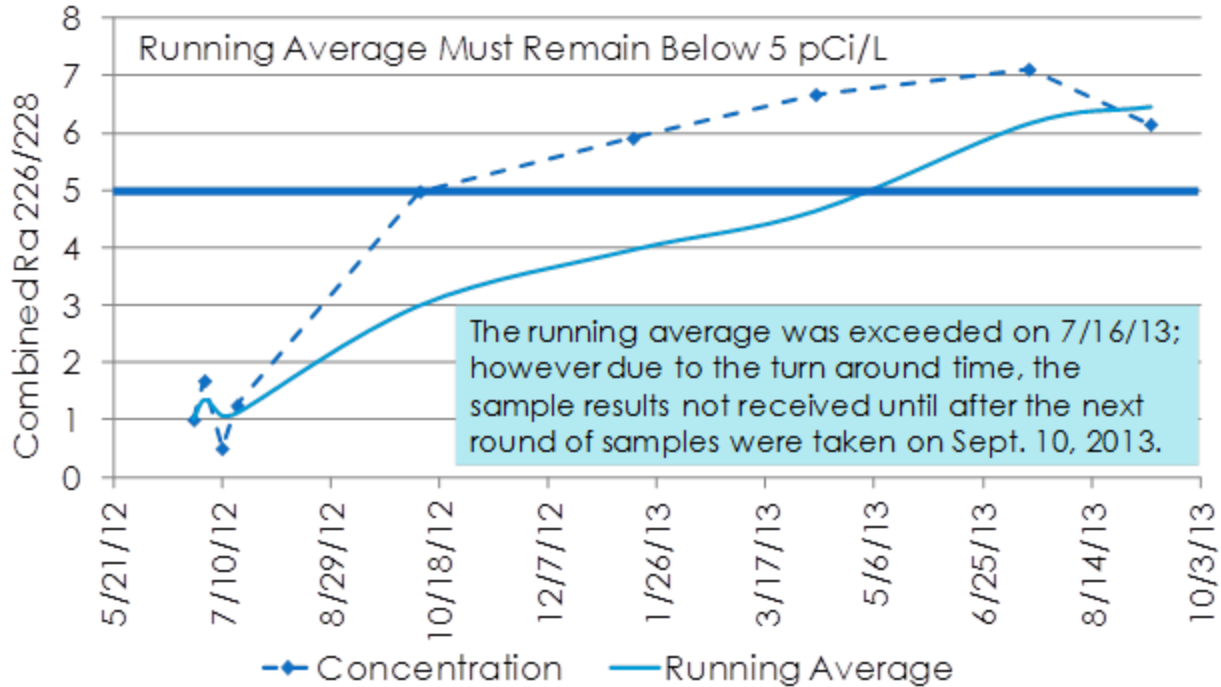
The initial water quality results from the first two months of water treatment plant operations showed just what was expected based on the laboratory and pilot testing. The plant was successfully treating all five critical water quality parameters and meeting the permit limits (see table below). However in October 2012 the water treatment plant operators observed that the combined radium 226/228 was higher than it had been at plant start up, but it was still just below 5 pCi/L. This happened in successive quarters: October, January, and July sampling dates. Plant operators had tried various ideas to improve the radium removal; adjusting the pH, adjusting the sodium hypochlorite feed; anything to try to mimic the conditions that occurred during the laboratory and pilot testing. But all of the efforts were to no avail. In July 2013 the 4-quarter running average of 5 pCi/L had been exceeded by 0.184 pCi/L and a Notice of Violation was issued by the Department on September 19, 2013 (see graph below). The long 6 to 8 week turn around time (time from sampling to results) for radium 226/228 testing proved to be a huge challenge. The delayed feedback made it very difficult for the operators to tell if their efforts had been effective.

Parameter	Well No. 8 Raw Water (Typ. Range)	Well No. 9 Raw Water (Typ. Range)	Finished Water (6/2012)	NJ Standard
Iron	3.7 - 4.6 mg/L	9.0 - 12.0 mg/L	0.03	0.3 mg/L
Manganese	0.09 - 0.11 mg/L	0.12 - 0.23 mg/L	0.002	0.05 mg/L
Aluminum	0.5 - 0.8 mg/L	1.0 - 1.9 mg/L	ND	0.2 mg/L
Radium 226/228	Up to 9.1 pCi/L	Up to 9.9 pCi/L	0.17	5 pCi/L
Benzene	0.87 - 0.89 ppb	0.76 - 0.90 ppb	ND	1 ppb

**Table: Water Quality at Plant Start Up**

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**Graph: Initial Radium 226/228 Data**

In September of 2013, following receipt of the N.O.V. Paulsboro voluntarily took Well Nos. 8 & 9 and the Water Treatment Plant off line until such time that a solution could be found and implemented. Paulsboro, Sickels & Associates, Inc. (water system engineer) and Hungerford & Terry, Inc. (filter manufacturer) began immediately to assess the situation and develop a plan to address the radium.

The water treatment process was designed to remove radium using a proven hydrous manganese oxide (HMO) process. The Paulsboro water treatment HMO process was designed to make use of the existing manganese in the raw water to co-precipitate radium. However based on the data obtained over the first year of operations we saw that the radium removal efficiencies had dropped off significantly. The reason for the ineffectual removal of radium was not fully clear. Although there was some speculation that the HMO formed in the settling tanks by the naturally occurring manganese was preferentially removing other positively charged ions, such as aluminum ( $Al^{4+}$ ), over the radium that had actually been targeted by the process.

In September 2013, immediately following plant shut down, a technician from Hungerford & Terry, Inc. (H&T) came to the plant to take samples of the GreensandPlus filter media. The media was analyzed microscopically and it was found to be in good shape, without loss of the manganese oxide coating, and without any blinding by iron and manganese. However it was going to take several more weeks to find out the results of the radium testing on the media.

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In the interim, Paulsboro, Sickels & Associates, Inc. and H&T were working together to assess possible causes and evaluate options for effecting greater removal of radium. One option that was on the table from the start was implementing a hydrous manganese oxide chemical feed. This was discussed at length at a meeting of the project team in mid-October 2013. This would entail installation of another chemical feed process, which would add the reactant (HMO) of a reaction between potassium permanganate and manganese sulfate. The HMO forms a floc to which radium adsorbs and then settles out of solution. Addition of the HMO is basically an enhancement of the naturally occurring HMO formed by the manganese in the raw water once it has been oxidized.

There were two additional pieces of information that helped to confirm the need to add the HMO feed to the treatment process. First, we received confirmation that the media had reached an equilibrium with radium and additional adsorption of radium onto the media could not be expected. This provided the first clue that the radium removal that was clearly observed during the first two months of operation may have been due either partially or solely to adsorption onto the GreensandPlus media. Second, the results came back from the water samples drawn on September 10, 2013. On that sample date, samples of both the raw and the finished water were taken. When the data came back in mid-October we found that the radium in the raw water had a concentration of 8.6 pCi/L and the finished water had a concentration of 6.15 pCi/L. While this reduction is not enough to bring the plant into compliance it did show that even though the media was saturated there was still some radium that was co-precipitating out with the oxidized manganese that was natural to the raw water.

The HMO system was then proposed to NJDEP and a temporary approval was given in November 2013. The system was designed and the order for the equipment was placed in the first week of January 2014. The equipment was then delivered in February 2014 and installed in February and March of 2014. The controls were set up in March and the HMO system began operation at the beginning of the second week of April 2014.

The initial impact of the HMO system seemed small. As stated earlier, the long lag time associated with radium water quality testing makes adjusting the system difficult. However, once the operational parameters were adjusted (ratio of  $\text{KMnO}_4$  :  $\text{MnSO}_4$  and feed rate), the operators were able to realize very effective radium removal. The results of the first combined radium 226/228 sample (taken on April 15, 2014) was 4.7 pCi/L. One month later the plant had a level of 2.2 pCi/L and the most recent data available, from June and July 2014, show that the combined radium 226/228 in the finished water has been consistently around 2.0 pCi/L, proving the effectiveness of the HMO process.

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**A Short Explanation of HMO Theory**

Currently the United States Environmental Protection Agency (USEPA) has set the maximum contaminant level (MCL) for combined radium at 5 pCi/L. Combined radium is typically made up of the isotopes 226 and 228. Although varied treatment methods, such as sodium cycle ion exchange and lime softening, are proven to reduce radium, these methods can be either too costly or not effective enough to meet desired radium removal goals. One alternative to traditional treatment methods is to introduce a hydrous manganese oxide (HMOs) into the feed water.

In pre-formed hydrous manganese oxides the HMO is typically formed by reacting potassium permanganate or sodium permanganate and manganese sulfate in aqueous solution to form a precipitate or floc of manganese dioxide (HMO).



HMOs, in contrast to other metallic oxides, such as iron oxides, have shown a strong ability to absorb radium. The affinity of the HMOs to absorb radium is due to their high surface area relative to their mass. By introducing HMOs in the feed water, raw radium can be adsorbed onto the HMO sludge and removed by filtration by coprecipitation with the manganese compounds. The filtration can be accomplished with traditional filter sand, although other filter media, such as GreensandPlus can also successfully reduce radium content. The process has shown efficiency in radium removal as high as 90%.

A key factor in the effectiveness of this method is the level of competing ions in the source water. Multivalent cations such as calcium, magnesium, barium, and aluminum have been proven to compete for absorption onto the HMOs and thus reduce the efficiency of radium reduction.

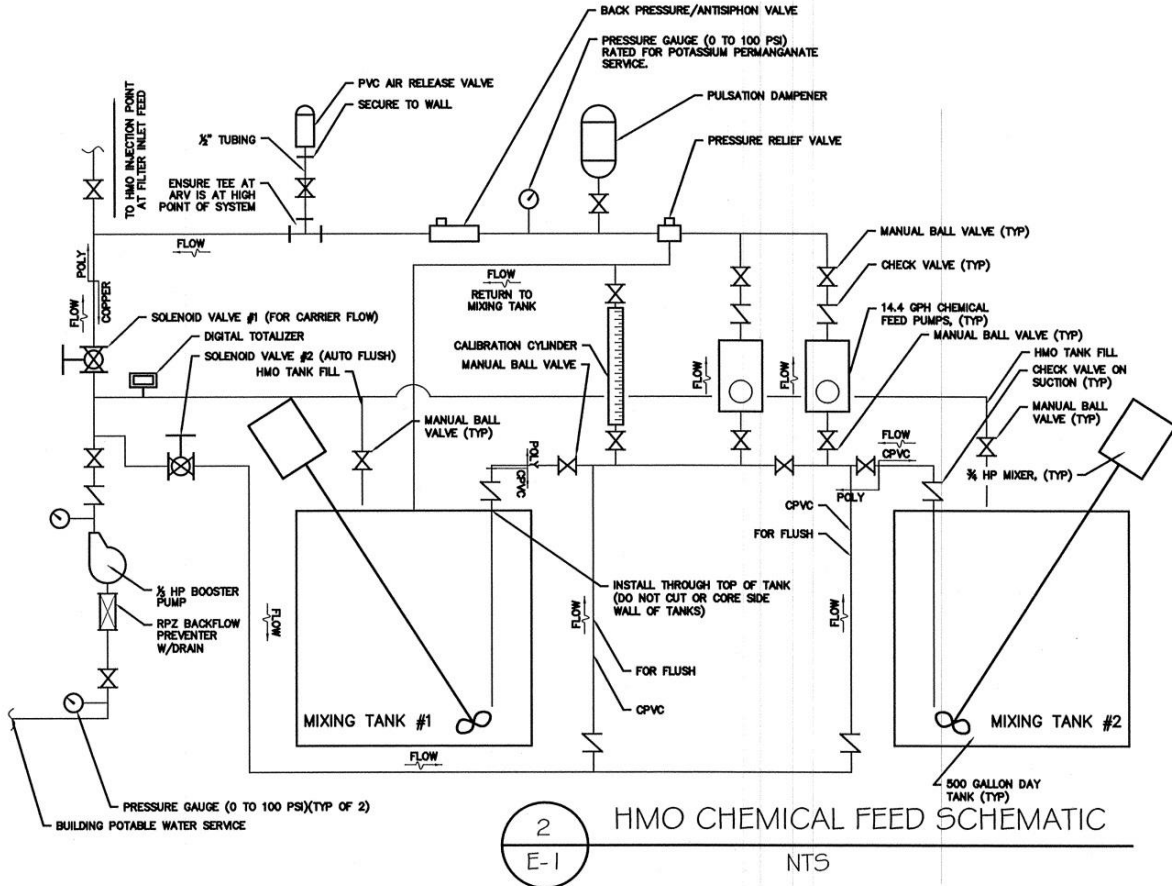
**The Pre-Formed HMO Chemical Feed System for Enhanced Removal of Radium 226/228**

The pre-formed HMO chemical feed system set up is fairly straight-forward. It is essentially two day tanks, along with the mechanical equipment necessary for mixing and delivering the HMO solution to the water upstream of the GreensandPlus pressure filters.

The schematic of the overall HMO feed system is shown in the sketch below.

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The dry chemicals are mixed in the 500 gallon day tanks. Each tank is meant to supply the HMO for an entire day with the plant at full operation (1,500 gpm or 2.16 MGD). When one tank is drawn down the second tank is brought online and the operators begin preparing a new batch of HMO. There are ¾ hp mixers installed in each tank to keep the HMO floc in suspension. The HMO is drawn from the day tanks using two positive displacement metering pumps run with variable speed drives and motors. The SCADA system flow paces the metering pumps based on the flow rate through the plant. The metering pumps then send the HMO to a carrier pipe that is flowing with potable water from the distribution system. The carrier water then takes the HMO to an injection point downstream of the high service pumps and just upstream of the GreensandPlus pressure filters.

The HMO chemical feed does not have a flow meter, however the flow can be determined by the rate and stroke of the positive displacement feed pumps. Information is monitored and recorded by the SCADA system. The HMO feed utilizes potable water as a dilution/carrier medium prior to injection into the process upstream of the primary



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GreensandPlus filters. There is a 1-inch potable water service that provides the carrier water and the supply to this potable water service is protected by a 1-inch diameter RPZ backflow preventer.

Once the HMO is injected into the process flow and mixes with the water, the radium ions get caught up by the HMO, co-precipitates, and is trapped by the pressure filter media. The floc with the radium is then removed when the filters are backwashed.

The dry potassium permanganate is stored in a separate room from the dry manganese sulfate. When a new batch is mixed they are introduced to the mixing tank only after the water has been added and only one chemical is added at a time. The potassium permanganate is added to the water first and is introduced at a slow rate until all of it has been added to the tank. The potassium permanganate crystals are then given sufficient mixing time to fully dissolve into solution. Only then is the manganese sulfate added. As with the potassium permanganate, the manganese sulfate is added at a slow rate to ensure that not too much is added at any one time. Since potassium permanganate and manganese sulfate react together, the slow addition also ensures that the reaction occurs at a slower pace. The HMO is then allowed to form in the day tank and the mixing facilitates the floc formation in addition to keeping the floc suspended.

**Operational Experience**

When the water treatment plant was restarted with the HMO feed as part of the process, there were several suggestions for how much HMO to feed and what ratio of  $\text{KMnO}_4$  to  $\text{MnSO}_4$  to use. There are no strict stoichiometric-type or empirical relationships of radium 226/228 removed to HMO added. Instead there are guidelines based on practical experience. These recommendations were based on prior experience by chemical suppliers and by Hungerford & Terry, Inc.

When the plant was initially started up again in April 2014, the HMO mix leaned more heavily on the potassium permanganate ( $\text{KMnO}_4$ ) than the manganese sulfate ( $\text{MnSO}_4$ ). This mix, which was indicated by prior H&T experience at other facilities, left more free permanganate to oxidize any remaining manganese in the raw water and to regenerate the oxidative charge on the filter.

Initial HMO mix: 74 lbs  $\text{KMnO}_4$  : 54 lbs  $\text{MnSO}_4$  : 512 gallons (mix remained purplish)

The operators then tried a mix that followed recommendations from Carus (a  $\text{MnSO}_4$  supplier). This mix did not leave any free permanganate, but instead reacted all of the permanganate with the manganese sulfate.

HMO mix (4/10/14): 74 lbs  $\text{KMnO}_4$  : 108 lb  $\text{MnSO}_4$  : 512 gallons (mix was brown)



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Since the initial startup the operators have made slight adjustments to the HMO mix per the Carus Batching Sheet. They have found that the following concentrations and feed rates are now very effective (feed rate of 3.9 gph for 650 gpm or 9 gph for 1,500 gpm):

HMO mix (current): 29 lbs  $\text{KMnO}_4$  : 46.5 lbs  $\text{MnSO}_4$  : 300 gallons of water (brown mix)

Typical doses that have been effective range from 0.5 to 1.0 mg/L of HMO as Mn (Carus Corporation). Paulsboro has found that the current feed rate of the specified mix is effective. This current HMO mix and feed rate yields a concentration of 1.0 mg/L of HMO as manganese.

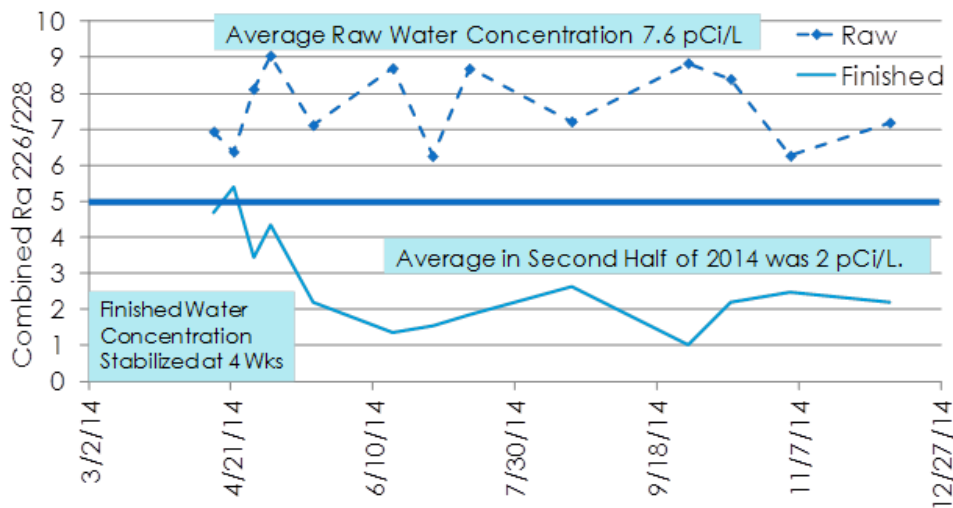
When the WTP is running at full capacity the plant will use 20.9 lbs/d of  $\text{KMnO}_4$  and 33.5 lbs/d of  $\text{MnSO}_4$  and the dosage will be 216 gallons per day where:

gallons per day of HMO solution = 9 gallons per hour x 24 hours = 216 gallons

lbs/d of  $\text{KMnO}_4$  = 29 lbs x (216 gallons / 300 gallons) = 20.9 lbs/d

lbs/d of  $\text{MnSO}_4$  = 46.5 lbs x (216 gallons / 300 gallons) = 33.5 lbs/d

The following graph provides a summary of the radium concentrations in the finished and raw water since the water treatment plant came on line. As can be seen from the data, there was a break-in period where the operators were troubleshooting the new equipment and controls in the first few weeks and the filters were acclimating to the addition of HMO. But after a month, the operations were continuing smoothly and the radium 226/228 in the finished water has remained low.



First sample taken on April 15, 2014. But results not received until May 22, 2014; 5 weeks later.

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**Construction & Operational Cost**

The construction of the HMO chemical feed process improvements was fast tracked and done under three contracts: equipment purchase, installation, and control system/SCADA upgrades. The total construction cost was approximately \$62,000.00. The cost of the chemical supply when adding 1 mg/L of HMO (as Mn) has been around \$ 0.157 per 1,000 gallons.

**Practical Lessons Learned**

The lessons learned on this “real world” project example would be specific to systems designed to treat for radium using HMO, but could also be more generally applied to other projects with similar constraints.

- It is important to cautiously interpret pilot data and be on the lookout for explanations or possibly other mechanisms beyond those that were initially theorized. Specifically when piloting an HMO system, it is important to ensure that the media is already in equilibrium with radium, or alternatively much longer pilot testing should be run, where the media would eventually become saturated with radium.
- When dealing with radium expect long lag times for obtaining sampling results. Also expect a few extra regulatory hurdles when permitting for a system to remove radiologicals.
- If radium is present along with high manganese, the naturally occurring manganese can be used as the HMO. However be aware that the presence of other positively charged metal ions can also compete for the HMO and be removed preferentially over the radium.
- When using a pre-formed HMO, such as the reactant of manganese sulfate and potassium permanganate, generally the HMO should be fully formed. The solution color should be brown with no free permanganate (the permanganate will give a purple tint). If extra oxidant is required, then operations will need to make adjustments to ensure that the HMO feed includes both the HMO and the required permanganate.

**Acknowledgements**

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