

II - LITERATURE REVIEW

It is obvious that no single tool or treatment method would suffice to produce a quality water. It is noteworthy, however, that potassium permanganate has the versatility required to produce a water having the quality characteristics most desired by the consumer. If the tap water is sparkling clear, without taste or odor, and will not stain porcelain fixtures in the household, it is immediately called "good water".

Undoubtedly, the plants that had used a limited dose of permanganate for removing iron and manganese did not realize that they were also simultaneously doing at least a partial job of taste and odor removal. The oxidation of iron or manganese from the soluble to the insoluble form by means of permanganate is almost instantaneous. If an excess of permanganate beyond what is required for the oxidation of iron or manganese is used, this excess will be available for the slower oxidation of taste - and odor - producing bodies which require a more prolonged contact time for odor destruction.

During the early use of potassium permanganate for water treatment, the technical grade was not only expensive but was also difficult to handle. The free - flowing material produced today is nonhygroscopic, noncaking, and of uniform crystals approximately the size of granulated sugar. It weighs about 100 lb. per cu. ft. is dustless, safe to handle, and can be kept indefinitely in dry storage. Dry, or in solution, it is odorless, noncorrosive and it does not produce harmful vapors. It can be handled by conventional methods and can be fed by the usual dry - feeder or positive displacement proportioning pump. It should be mentioned that, as potassium permanganate is not compatible with rubber, any pump diaphragm or hose line should be made of plastic. Metallic pipelines are entirely satisfactory

for transporting permanganate solution.

Iron and Manganese Removal

Soluble iron and manganese exist in raw - water supplies in the bivalent state - that is, as ferrous iron, manganous manganese. The most common salt of these metals in natural waters is the bicarbonate. The CO_2 in the bicarbonate originates from the natural decomposition of organic matter. It is also known that vegetation decomposes in lakes, impounded streams, and reservoirs, the manganese dissolves in the water if reducing conditions exist.

In order to remove soluble iron and manganese, or oxidation process is employed. This converts the soluble bivalent forms into the insoluble oxidized forms. In essence this is a reversal of nature's process for putting these elements into solution in the first place.

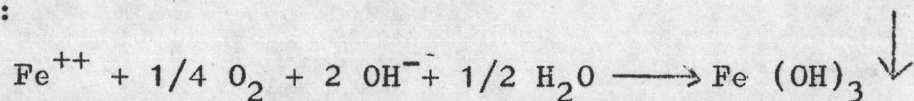
The methods that may be used for oxidizing the soluble forms of iron and manganese to their insoluble forms in order to precipitate them for removal by coagulation and filtration are listed below.

1) Aeration

Most of the treatment methods in use today is the removal of iron from water supplies which depends upon the oxidation of the soluble ferrous iron to the insoluble ferric form. The most commonly used oxidizing agent is oxygen, which is added to the water through aeration. In practice, aeration may be accomplished by:

1. open devices over which the water flows by gravity, with or without counter - current forced draft, eg., coke trays, slag trays.
2. spray devices which spray the water into the air.
3. diffused aeration, and
4. aspirator devices, eg., Venturi devices.

R.S. ENGELBRECHT, J.T. O'CONNOR and M. GHOSH reported that the most common method of aeration in Illinois is the coke tray aerator. The aerator is usually followed by a reaction or settling basin prior to filtration. The reaction of ferrous iron with oxygen leads to the formation of ferric oxides or hydroxides, according to the basic equation:



Stoichiometrically, 1 mg/l of oxygen will oxidize 7 mg/l of ferrous. It is believed that the oxidation of ferrous iron proceeds step wise through various ferrous - ferric hydroxide species.

The studies on the oxygenation of ferrous iron, STUMM and LEE found the rate of oxygenation to be a function of the ferrous iron concentration and the partial pressure of oxygen (Po_2):

$$-\frac{d(\text{Fe}^{++})}{dt} = K' (\text{Fe}^{++}) \text{Po}_2$$

In their study of the effect of pH on the rate of oxidation of ferrous iron, their data indicated a 100 - fold increase in the rate with an increase of one pH unit. Because of this second order relationship with respect to hydroxyl ion concentration, the overall rate was expressed as:

$$-\frac{d(\text{Fe}^{++})}{dt} = K (\text{Fe}^{++}) \text{Po}_2 (\text{OH}^-)^2$$

where

$$K = \frac{K^1}{(\text{OH}^-)^2}$$
$$K^1 = \frac{K_0}{\text{Po}_2}$$

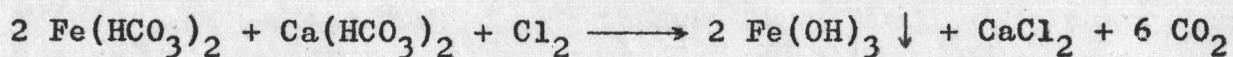


$$K_o = \frac{- \ln (Fe^{++})}{dt} \quad 004559$$

and $K_o =$ logarithm of the rate constant.

Iron can be more readily removed by aeration, except for the last traces or if it is present as an organic complex.

2) Chlorine or Hypochlorite Chlorine or Hypochlorite are effective for oxidizing of iron to insoluble forms even at low pH values. The reaction may be represented as:



From this equation, it can be calculated that 1.6 mg/l of chlorine are required to oxidize 7 mg/l of iron. A.W.W.A.(1951) reported that chlorine acted in two independent ways: first, it destroys the complex compounds of iron and manganese, and thus modifies them so that they may be readily oxidized; second, either the chlorine or the dissolved oxygen, chlorine dose may be reduced through partial oxidation. Although chlorine and hypochlorites can be used in a more rapid process than aeration, but they are not efficient in oxidizing manganese and organically bound iron and manganese.

3) Adjustment of pH is economically feasible and/or effective means of iron and manganese removal if lime or lime-soda softening is practiced at pH range above 9.5 .

4) Catalysis, using a variety of catalysts, particularly the copper iron is known to enhance air oxidation.

5) Ion - exchange resins are effective in removing small quantities of soluble iron or manganese, but they become quickly fouled by the oxide when they are used for treating water containing large quantities of contaminants.

6) Chlorine dioxide is a strong oxidizing agent

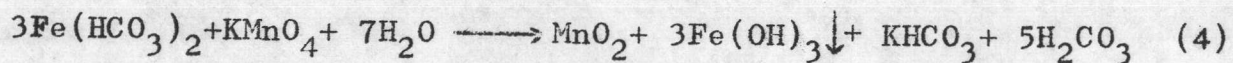
that will rapidly oxidize iron and manganese to their insoluble forms. Because of cost considerations it is seldom used for oxidizing soluble iron, although it is used to some extent for the oxidation of the last traces of soluble manganese.

7) Manganese dioxide and potassium permanganate offer an effective method when manganese dioxide is affixed to greensand. The manganese dioxide is effective for removing soluble iron and manganese up to the point where it has been degenerated to manganic oxide (Mn_2O_3). It then becomes necessary to regenerate manganese dioxide by batch treatment with a solution of potassium permanganate. The principal economic disadvantage of a regenerate manganese dioxide by batch treatment with a solution of potassium permanganate. The principal economic disadvantage of a regenerative batch process is that a substantial excess of permanganate is required. This disadvantage can be overcome through the use of a regenerative process using a continuous feed of potassium permanganate solution ahead of a filter containing a layer of an anthracite filter medium superimposed upon a bed of manganese treated greensand. In this way, full advantage is taken of the oxidation potential of potassium permanganate as compared to manganese dioxide. If the amount of soluble iron and manganese is high in relation to the amount of permanganate being fed, then the manganese treated greensand removes the excess by the "degeneration" reaction of the batch process. Conversely, if the permanganate solution being fed is in excess of that required by the soluble iron and manganese, then the manganese - treated greensand consumes the excess permanganate and thereby automatically regenerates itself.

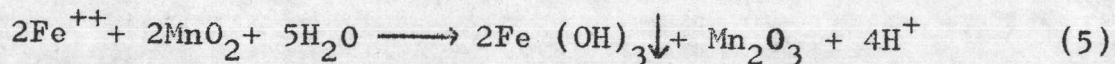
The anthracite filter medium on top of the manganese - treated greensand increases filter runs because it removes the bulk of the insolubles without binding the filter media. Control is obtained by means of a sample cock at the base of the filter layer.

The potassium permanganate feed should be adjusted so that a slight increase will show a pink color at the sampling point.

8) Potassium permanganate WILLEY and JENNINGS (1963) discussed the use of potassium permanganate (KMnO_4) to oxidize ferrous iron to insoluble ferric precipitate. They suggested that dissolved iron and manganese can be effectively removed from water by continuous feeding of potassium permanganate to water before it is passed through a manganese green sand filter. This method has been known as a continuously regenerating process. The quantity of potassium permanganate required can be determined by running a permanganate demand test on the water to be tested. The reactions involved are:



Theoretically, one part of potassium permanganate (KMnO_4) will oxidize 1.06 parts of soluble ferrous iron to insoluble ferric iron. In practice, it was found that a less amount of potassium permanganate was required due to the secondary reaction of the MnO_2 formed, according to the following equation:



They also developed a permanganate demand curve for oxidation of ferrous iron completely in the given concentrations.

In certain cases, it might be advantageous to aerate or prechlorinate before oxidizing with potassium permanganate. With a combination treatment, the easy - to - oxidize iron is oxidized by aeration or prechlorination while the remaining more difficult - to - oxidize or organically bound material is readily oxidized by the permanganate. In all cases

potassium permanganate alone will oxidize all forms of soluble iron and manganese, so the above is suggested merely as a possible economy measure. Oxidation by prechlorination ahead of permanganate, however, should not be carried out if organic contaminants are present, particularly phenolic compounds which when chlorinated will give rise to the formation of chloro - derivatives that create serious taste and odor problems.

Taste and Odor Control

By definition "quality water" should have a threshold odor number of 2 or less as determined by the odor - free water dilution method at a temperature of 60° - 65°C. This would represent an ideal water from the odor standpoint but, depending upon the nature of the odor, a threshold of 3 or even 4 might never be noticed by the consumer.

The numerical threshold value of raw water is not a direct indication of the difficulty encountered in reducing the odor to a palatable level. There are raw waters with threshold values of 7 or 8 which were more difficult to treat than other raw waters having threshold values in the range of 20 - 30 or even higher.

Oxidants other than potassium permanganate have been suggested for destroying tastes and odors in water supplies. These are represented by ozone, chlorine dioxide and chlorine. Ozone and chlorine dioxide are very similar in their action. Both are unstable gases which supply nascent or active oxygen. As these substances are gases, the reaction must be complete before they flash from the zone of action.

When chlorine is used for the oxidation of impurities, it does not only oxidize but also chlorinates, and, in most cases, the chloro - derivatives which are formed are more objectionable than the original taste - and odor -

producing compounds. This is especially true of cyclic compounds containing a benzene ring structure - for example, phenol and cresol. Such chlorinated compounds are much more difficult to oxidize further by a strong oxidant like potassium permanganate. They are also more difficult to adsorb by a material such as activated carbon. These chlorinated compounds are responsible for what might be called a chlorinous odor, as differentiated from a chlorine odor. It is expedient to delay the application of chlorine for disinfection purposes until after the application of permanganate.

It has been said that potassium permanganate eliminates taste and odors by means of oxidation and adsorption, but this statement requires some clarification. Although potassium permanganate is an extremely strong oxidizing agent, the permanganate itself is not an adsorbing agent. It is the complex insoluble manganese oxide hydrates, formed during the oxidation process, that act as adsorbents. The role of the manganese oxide hydrates in minimizing the potassium permanganate, requirements for iron and manganese removal has already been discussed. This action might be accounted for by the adsorption of bivalent iron and manganese. Similar complexes are feasible and might loosely be called "adsorption" when removing organic taste - and odor - producing materials.

W. ARTHUR WELCH reported that potassium permanganate is applied as a solution, either from dry feed or solution feed, and is very easy to control. The strong oxidizing action of permanganate is prolonged owing to the persistent release of oxygen in the zone of chemical action. The time required for the optimum dose of permanganate to do its work varies from one water supply to the next. As little as 10-15 min may be sufficient in one case, whereas, with contaminants difficult to oxidize, the time may be longer and the optimum dose is higher.

The use of chlorine may result in the development

of a chlorinous odor in water where no odor existed. As an example, a raw water with an odor value of only 2 was encountered in Virginia. The chlorine demand was 6 ppm, but after applying this dose of chlorine and then dechlorinating, there was a residual chlorinous odor of 6.

This same raw water was treated with potassium permanganate in the amount of 1.75 ppm, after which the chlorine demand was nil. When the permanganate - treated water was chlorinated to 1 ppm free residual, the resulting threshold odor was 1.2, and it was not chlorinous. As a matter of fact, in any of the various plants where permanganate is being used in pretreatment, it is possible to carry a free chlorine residual of 1 ppm or more and neither a chlorinous nor a chlorine odor will be detectable.

An impounded water supply in eastern Pennsylvania had a chlorine demand of only 3 ppm for breakpoint. The permanganate demand for this same water was 1.5 ppm. This tends to show that the nature of the impurities in this water was such that the chlorine was functioning almost entirely as an oxidizing agent and not forming chlorinated compounds, because there was very little chlorinous odor discernible. The threshold odor of this raw water was 24 and it was reduced to 1.4 with either chlorine or permanganate at the doses mentioned.

Another water supply in Virginia required chlorine in the amount of 10 ppm, which brought the odor of the raw water from a value of 24 down to a value of 8. This value of 8 was determined on dechlorinated tap water. Free - residual chlorination was replaced by permanganate in the amount of 2.75 ppm and the odor was reduced to a value of 2. Incidentally, the color of this water was reduced from 50 to 4 with the dose of permanganate mentioned.

In Pennsylvania, a river supply having a threshold

odor of 12 required chlorine in the amount of 10 ppm. Free - residual chlorination reduced the odor, which was very chlorinous in nature, from 12 to a value of 8. This same water when treated with only 1.5 ppm permanganate had an odor value of 1.4, which was nonchlorinous. This example is used to show a case where the chlorine being applied was doing a very good job in producing chlorinous compounds, as inferred from the fact that such a low dose of permanganate was required for straight oxidation.

The preceding examples illustrate the advantage of using permanganate as a preoxidant and applying chlorine subsequently as a persistent sterilizing disinfection agent.

Economic Considerations

Quality in any product implies a premium price. When potassium permanganate is used as a tool for producing quality water, this is not always the case. Often the savings involved, through the elimination of high doses of prechlorine, chlorine dioxide and activated carbon, equal or outweigh the cost of permanganate. Naturally, there would be no saving involved if no previous attempt had been made to produce a quality water by other means.

As an extreme example, the raw water for a plant on the Ohio River had a threshold value of 14. This odor was reduced to 5 by the application of 22 ppm of activated carbon. When permanganate in the amount of 2.5 ppm was substituted for carbon, the odor was reduced to a value of 2 and the daily saving amounted to a value of 2, and the daily savings amounted to approximately \$ 144 on the basis of an average daily pumpage of 17 million gallons. These figures were obtained in actual plant application, but it should be emphasized that this is an extreme case for illustrative purposes.

There might be isolated cases where a combination

of potassium permanganate and activated carbon is required to produce a potable water. A case of this type was reported in Cedar Rapids, Iowa during the summer of 1961.

Dosage Control

Dosages can be readily controlled by the highly sensitive and extremely convenient visual technique. As the permanganate is consumed, the water color changes from pink to brown, showing at a glance that permanganate is at work. By observing the sedimentation basin, a color zone can readily be seen. This zone should be established about one - half to three - quarters of the way through the basin. If the potassium permanganate demand of the water increases, the color will retreat toward the point of permanganate addition; if the demand decreases, the color zone will advance toward the filters. The dosage should be adjusted to maintain a residual color at a predetermined position in the basin as indicated by experience.

An instrument is being developed to monitor the concentration of residual potassium permanganate. This device will indicate and record the potassium permanganate on a chart in parts per million and should prove a valuable tool in controlling the addition of the potassium permanganate to the water. The instrument will be exceptionally useful for those plants in which the basins are covered - in remote locations or are of the upflow type. The principle of measurement is based on the formation of an intense yellow color in the reaction between orthotolidine and potassium permanganate. The intensity of this color is then continuously measured photoelectrically.

Slow Sand Filtration

Slow sand filters are able to cope with raw water turbidities of 100 - 200 mg/l for a few days, the turbidity should not rise above 50 mg/l for a longer period. The best

results can be obtained when the average turbidity is less as 10 mg/l while excellent results can be obtained when the turbidity drops below 2 mg/l (measured as SiO_2). When working ideally, these filters have been shown to reduce total bacterial counts by 99.9 to 99.99% and E. Coli by 99 to 99.9%.

Slow sand filtration rate varies from less than 0.1 to about $0.4 \text{ m}^3/\text{m}^2/\text{hr}$ and is so small that only after an extended period of service, a few weeks to a few months, cleaning is necessary. The filter bed composed of fine grains, effective diameter between 0.15 and 0.35 m.m suspended and colloidal material from the raw water are kept in the top of the filter bed. Cleaning of a slow sand filter is performed by scraping off the upper one to a few centimeters. Two important parameters appeared to be considered, the filtration rate and the length of filter run.

Alternative Media for Slow - Sand Filters

AWWA (1965) stated that the finer sand may be shallower than coarse sand but the former produces greater head loss and clog quickly than the latter. The depth of sand can cause flow resistance and additional cost. It is therefore recommended that the size of the sand and depth should not be finer and larger than that necessary to provide a good efficiency and low head loss.

BALLEY (1939) performed a study of using anthracite coal in a slow filter as a filter medium at the Eastman Kodac Company's water purification plant. An experiment with "Anthrafilt" was performed by replacing the top four (4) inches of sand with washed Anthrafilt, an effective size 0.40 - 0.45 m.m, and a uniformity coefficient of 1.4. Each grain of Anthrafilt was approximately twice the size of each grain of sand of the same weight, in reality, that is a roughing filter on top of the regular sand filter. He has shown that Anthrafilt was strong enough to withstand the rough cleaning action without breaking down and it was found that there

was considerable mixing of the sand and Anthrafil to a maximum depth of eleven (11) inches. There was no loss of large particles of Anthrafil in wash water except very fine particles down of during the first few washings. An equivalent out put was obtained for washing the Anthrafil unit one - third as often as a regular unit and the rate of this unit had no effect upon the turbidity of the effluent.

SEVILLA (1971) studied water filtration using burnt rice husk and others local materials. In preliminary test runs two levels of filtration rate were studied: semi - rapid rates of 2.5 and 1.25 m³/m²/hr. Results of the test runs, the maximum filtration rates for the burnt rice husk media to achieve an efficient turbidity of 5 FTU or lower at the highest turbidity loadings of about 1000 FTU were 1.25 m³/m²/hr. Burnt rice husk removed turbidity so efficiently at any level with a defined head loss that a secondary filter might not be needed if it was found reliable in terms of chemical and biological effects. Because of the difficulty in cleaning filter media, burnt rice husk after using, it was more practical to discard them at the end of filter run.

SEVILLA (1971) also stated that the most effective local media to remove colour and turbidity was burnt rice husk. No media seemed to be superior than the other if they were considered not only removal efficiency but also length of run.

Although burnt rice husk shows the best efficiency in turbidity removal, colour and length of run, bacteriological and chemical effects need to be investigated.

Design of Experimental Filters

GHOSH (1958) investigated the effects of the physical characteristics of the media when applied to filtration of turbid water, with particularly reference to loss of head and removal of turbidity at different depths under different

condition of flow, using media of different size and without the case of chemical coagulants. The experimental filter consists of a 1/4 in. thick perspex tubing, 3 1/2 in. internal diameter, 5 ft long. The under drainage system was circular 1/2 in. thick perforated plate. The depth of filter media used was 30 in., and there was a constant head of 27 in. of water over top surface of the filter bed. A manometer was connected to measure head loss from a point of few inches above the top surface of the media and then from different depths of bed.

