## Water Treatment

Iron (Fe), Manganese (Mn), and Hydrogen Sulfide ($H_2S$) can present a very complex challenge to water treatment. The combination of these contaminants is sometimes referred to as the "troublesome trio." In Canada and the United States, the maximum permitted concentrations in drinking water Fe is 0.3 ppm, 0.05 ppm for Mn and $H_2S$ being a gas state is limited to 3 threshold odor numbers and still not regulated by Environmental Protection Agency (EPA) [1 ppm= 1 mg/L]. The same treatment method used for reduction of one contaminant can often be applied to all three. However, due to the complexity of water chemistry, there can be variations in the treatment scheme. There are many treatment methods, which can be used for the reduction of all three contaminants.

1) Ion exchange - Cationic and Anionic resin
2) Aeration plus filtration - Using atmospheric pressurized aeration followed my multimedia or filter media like sand
3) Chemical oxidation plus filtration - Using oxidants such as Chlorine (Cl), Potassium Permanganate ($KMnO_4$), Ozone ($O_3$), Hydrogen Peroxide ($H_2O_2$)
4) Catalytic oxidation filtration - Manganese Dioxide ($MnO_2$) based media

For the purpose of this article, we will be specifically discussing $MnO_2$ based media. $MnO_2$ based medias for Iron, Manganese and Hydrogen Sulfide reduction have been in use since World War II. Greensand (more recently named Greensand Plus) was the most common media used for the reduction of the three contaminants. However, with recent advancement in technology, Greensand Plus has been losing its charm, primarily because of the high regeneration cost associated with the media and diminishing amount of support core material (example: glauconite) needed for coating the oxidizing $MnO_2$ layer. The media uses $KMnO_4$ for regeneration. This chemical is expensive, hazardous and has a high maintenance cost.

There are two kinds of MnO2 based medias as follows;

1) Manganese Dioxide coated media with a support base – i.e. Birm and Greensand Plus*
2) Manganese oxide solid mined ore – specifically CCG MAG-50

For the intent of this article, we will be doing a comparison between Birm, Greensand Plus, and CCG MAG-50.

**Birm is a trademark product of Clack Corporation; Manganese Greensand is a trademark product of Inversand Company; CCG MAG-50 is a trademark product of Continental Carbon Group.*

## How do MnO2 based medias work?

$MnO_2$ based media are capable of doing two important operations. First, they oxidize the iron into particulate form and then these particulates are trapped within the media bed utilized. Upon backwash, the particulates are reduced from the media bed.

If the water also has hardness ions present, it is recommended to reduce iron before you reduce water hardness. Iron in dissolved form ferrous iron ($Fe^{2+}$) is usually associated with carbonates. When the iron passes through the bed of iron reduction media, the iron gets oxidized to Ferric ($Fe^{3+}$) and forms insoluble particulates of rust (Ferric Hydroxide, $Fe(OH)_3$). The $MnO_2$ based media acts like a catalyst in the process. A catalyst is a substance, which increases the reaction rate without itself changing in any chemical form. Similar to iron, manganese in dissolved state is manganous ion ($Mn^{2+}$) and is converted to insoluble manganese ($Mn^{4+}$) ion. Hydrogen Sulfide gets reduced to yellow sulfur particulate. The conversion reaction is dependent on the pH of raw water.

## Media Operating Parameters and Individual Analysis

The table below shows some of the key parameters for Birm, Manganese GreenSand and CCG MAG-50:

| Operating Parameters (per cu.ft) | Birm | Greensand Plus | CCG MAG 50 |
|---|---|---|---|
| pH | 6.8-9.0 | 6.2-8.5 | 6.5-9.0 |
| Service Flow rate (gpm/sq.ft)** | 3.5-5 | 2-12 | 5-12 |
| Backwash Rate (gpm/sq.ft)** | 10-12 | 12-15 | 25-30 |
| Bulk Density (lbs) | 36-38 | 88 | 115 |
| % $MnO_2$ conc. | 1.0 | 0.5-3.0 | 80+ |

***Service and backwash rates are based on different water temperatures (4-27 degree Celsius). When water is cold, it is more viscous and has higher density. Hence, a lower gallon per minute (gpm) amount of water is required per square foot (sq. ft) for backwash and vice versa for higher water temperature.*

*Birm* - This is a light media and hence requires low backwash water. However, presence of dissolved oxygen (DO) is very important for the operation of this media. DO content of at least 15% and 29% is needed for iron and manganese reduction respectively. Hydrogen sulfide cannot be reduced using Birm media. Free chlorine in the water should be less than 0.5 ppm in concentration, as this can affect the media layer coating. No chemicals are needed for the regeneration of this media.

*Manganese Greensand* – Again because of the manganese coating, this is a light media as well. In this case, $KMnO_4$ is needed to regenerate the media, so that the original oxidizing power of media layer is at full strength. The media can be used in two methods of operation: continuous regeneration (CR) and intermittent regeneration (IR). The CR method is recommended for predominantly iron bearing waters with or without the presence of manganese, and the IR method is recommended for use on ground waters in which manganese predominates. The capacity of reduction of this media depends on the $KMnO_4$ dosage.

*CCG MAG-50*- ORP (oxidation reduction potential) plays a very important role in operation. It is recommended that the ORP of the water to be treated is at least -170 mV; otherwise more oxidants need to be added. Chlorine is the most common oxidant. However, it is recommended that not more than 4 ppm of free Chlorine be added into the water as it may destroy the media. Being a very heavy media, backwash is extremely important in the effective operation of this media. Optimum

backwashing makes sure that the mined ore granules rub against each other to create attrition so that a fresh layer of $MnO_2$ is available for operation.

Reduction capacity of the three medias for individual contaminants per cubic ft is given in a table below:

| Contaminant | Birm | Greensand Plus*** | CCG MAG-50 |
|---|---|---|---|
| Iron | 8 ppm | 1ppm using 1 ppm $KMnO_4$ regent | 10 ppm |
| Manganese | 6 ppm | 1ppm using 2 ppm $KMnO_4$ regent | 5 ppm |
| Hydrogen Sulfide | Not compatible | 1ppm using 5 ppm $KMnO_4$ regent | 3 ppm |

****Using continuous regeneration (CR) method.*

*Note: For Birm and CCG MAG-50 pilot studies need to be conducted if more than one contaminant is present in water.*

**Observations**

From the above literature each media has its own pros and cons depending on the water chemistry of the raw water. However, following points can be noted from the above discussion:

- In terms of bulk density CCG MAG-50 is the heaviest media and hence requires more water for backwashing compared to Birm and Greensand.
- CCG MAG-50 has the best contaminant reduction efficiency primarily because of its very high purity of manganese dioxide.
- Birm cannot be used in presence of any oxidants as this can hamper its performance, which is not the case with Greensand or CCG MAG-50 (but in limited quantity).
- The pH range for operation of all medias is almost identical.