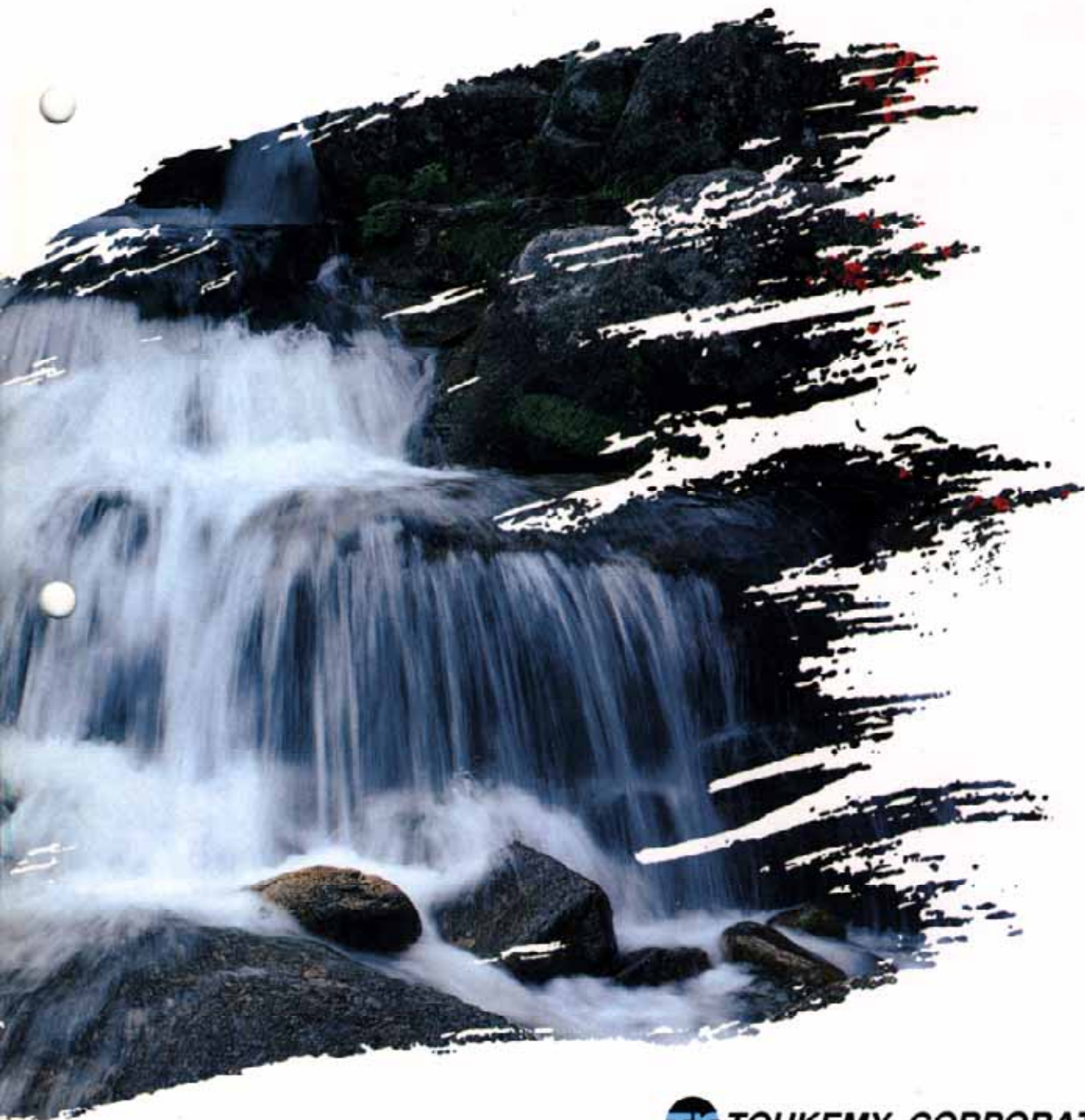


For Iron and Manganese Removal

CATALYTIC OXIDATION FILTER MEDIA

FERROLITE MC.GC.SC
TOYOLEX F
MANGANESE SAND.



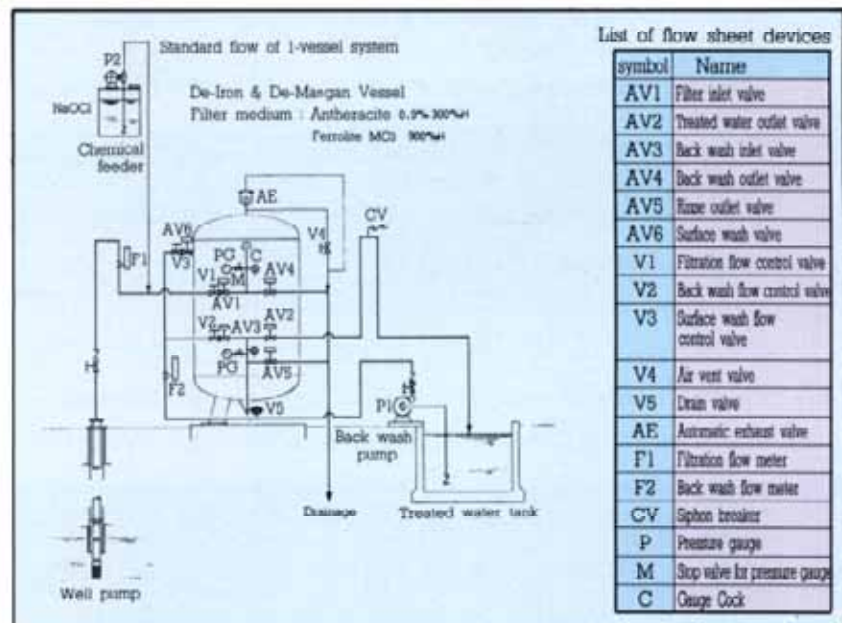
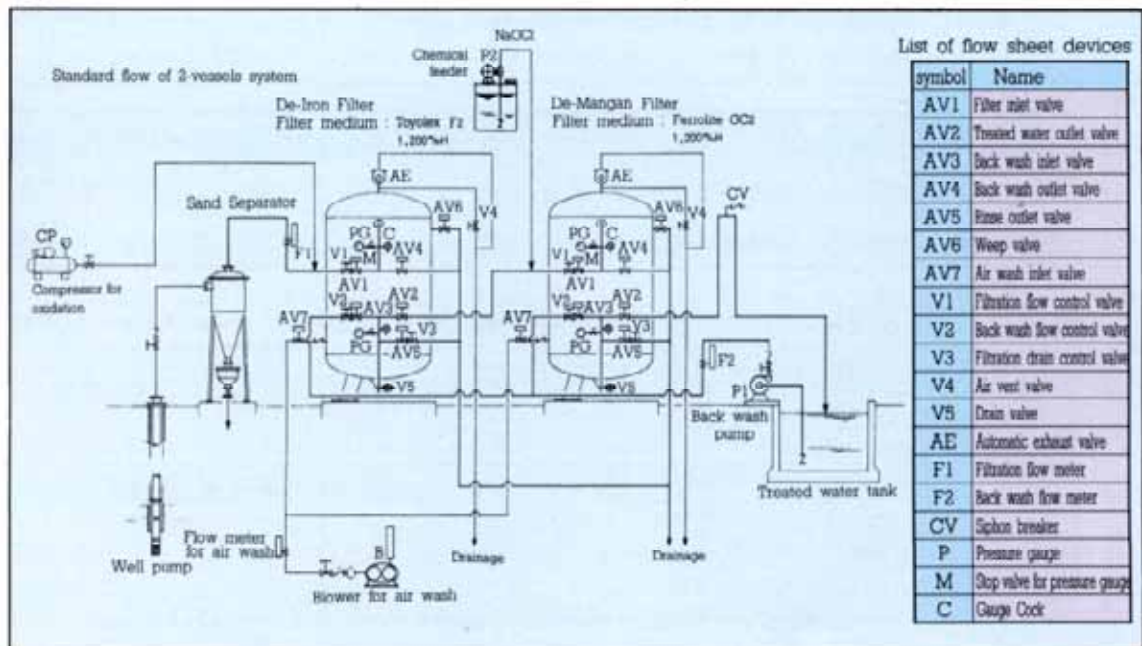
TIC TOHKEMY CORPORATION

CATALYTIC OXIDATION FILTER MEDIA

D. Standard Catalytic Oxidation Treatment

When performing catalytic oxidation treatment for iron and manganese removal, good results can be obtained by using S.V. (water quantity/filter medium quantity/hr) 10hr^{-1} as a standard and determining L.V. and the kind of filter media according to the water quality. The standard flow sheet is shown in Fig.2.

Fig.2. Standard Flow Sheet of Filter Media for Iron and Manganese Removal



B. Toyolex F

Toyolex F series have been developed particularly for application with oxidation by air and these filter media are effective especially for underground water with great iron content.

Though some time should be taken for trial operation in order to reforming the hydroxide iron coated on the filter media into the suitable form of the hydroxide iron in the water, because of largely saving running cost due to using natural air as oxidizer, these filter media are suitable for treatment of industrial water, general service water and drinking water which are used in large quantities.

Air as oxidizer is fed before the filter plant so that oxygen will dissolve well in raw water. Then, when the raw water comes in contact with the filter media which function as oxidation catalyst, oxidation and removal are immediately performed. As the oxidizing power of oxygen in the air is inactive compared with chlorine and sodium hypochlorite, the filter plant system should be so designed that air will well mix with raw water and that a sufficient reaction time will be secured, by which good treatment can be performed. However, when a large quantity of dissolved silica is contained, reverse reaction (iron getting colloidal) is caused. In the case of raw water which contains a large quantity of free carbonic acid and bicarbonate, discharge carbon dioxide gas into the air. When pH value is low (6.5 or less), adjust pH value before treating water.

C. Raw Water Requiring Pre-treatment

The following conditions should be met to perform catalytic oxidation of raw water taken directly from the well: dissolved silica content being 40 mg/ℓ or less, hydrogen sulfide content being 0.2 mg/ℓ or less, iron content being 20 mg/ℓ or less, KMnO_4 consumption being 15 mg/ℓ or less, acid consumption being $[40 + 1.8(\text{Fe} + \text{Mn})]$ (mg/ℓ) or less and pH value being 6.5 or more. There are some cases where pre-treatment is required due to a large quantity of free carbonic acid, silica, ammonia nitrogen organic substances and humic acid being included. Aeration, pH treatment, microfloc treatment, break-point treatment, oxidation treatment by H_2O_2 or KMnO_4 , etc. are employed as pre-treatment methods. By performing pre-treatment to meet the conditions for catalytic oxidation, it becomes possible to stabilize the quality of treated water and to maintain the activation and perpetuity of filter media.

CATALYTIC OXIDATION FILTER MEDIA

3. pH Value of Raw Water

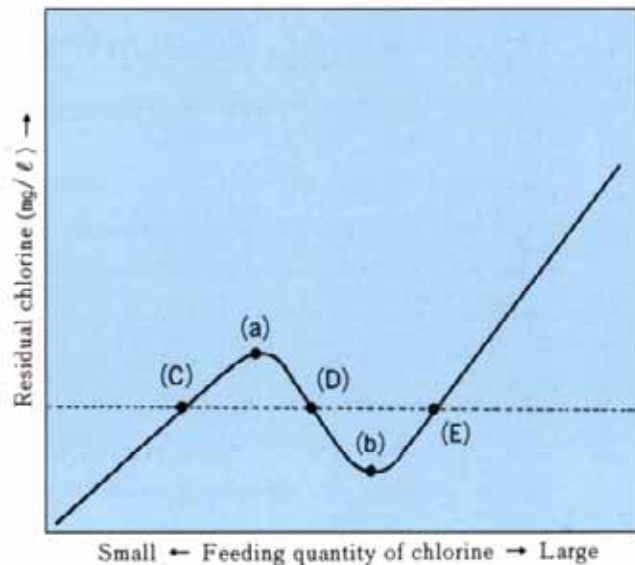
In principle, it is desirable that pH value of raw water is higher than 6.5.

If pH value is lower, the film may lose its oxidizing power, and dissolve in water and run off together with filtrate. In such cases, pH value should be adjusted so that it will be higher than 6.5 before using raw water.

4. When Raw Water Contains Ammonia Nitrogen

When chlorine is fed to raw water containing ammonia nitrogen, first the ammonia in raw water reacts with the chlorine, yielding chloramine (combined chlorine). With the feeding quantity of chlorine increasing, the quantity of residual chlorine increases to reach the maximum value at a certain point [point (a)], and starts to decrease after that. Then, the quantity of residual chlorine reaches the minimum point [point (b)], after which it increases linearly in proportion to the feeding quantity of chlorine.

Fig.1 Break-point Chlorination



The residual chlorine before point (b) in the figure is all chloramine (combined chlorine). For oxidation treatment in deferrizing and demanganatizing, the residual chlorine after point (b) [residual free chlorine of 0.3 ~ 0.5mg/l at point (E)] is needed.



5. How To Use Our Filter Media

A. Ferrolite MC, GC and SC and Manganese Sand

1. Feeding Chlorine or Sodium Hypochlorite (CL-prefeeding Method)

If reducing substances are contained in the water, there is a possibility that the manganese film dissolves in the water and runs off together with the filtration. To prevent this from happening, chlorine or sodium hypochlorite is continuously fed to activate the filter media. Ideal activation can be expected if the system is so designed as to feed the above additive not immediately before the filter plant but near the well or intake and to allow the additive to mix well with the raw water on its way to the filter plant.

Although a relatively large feeding quantity of chlorine or sodium hypochlorite is required to the newly filled filter media owing to activation of manganese film, the required feeding quantity of the said additive during normal operation of filter plant is theoretically 1.29 times the manganese content (mg/ℓ) or 0.64 times the iron content (mg/ℓ) of the raw water.

However, depending upon quantities of organic matter, ammonia and reducing substances contained in the raw water, it is necessary to add more feeding quantity to the abovementioned theoretical quantity.

As for the general guide line on feeding quantity of chlorine, if the feeding is done so that the quantity of residual free chlorine of the treated water immediately after the raw water passed through the filter plant becomes $0.3\sim 0.5 \text{ mg}/\ell$, this is the most effective and practical.

2. Layer Thickness and Flow Velocity

Normally the layer thickness of filter medium is about 1.2 m and the flow velocity is $10\sim 30 \text{ m}/\text{Hr}$, depending upon the turbidity, iron and manganese contents, and contents of humic acid, silica, etc. of the raw water. In the case where the flow velocity is to be accelerated, in principle, it is necessary to take a larger layer thickness in order to secure a sufficient space velocity (time for catalytic oxidation).

In this case, different from mere turbidity filtration with filter sand or anthracite media, space velocity as well as line velocity should be taken into consideration in designing of the filter plant system.

Iron and manganese are co-existing in nearly every underground water, and chemical iron is oxidized first and manganese is oxidized after that. Therefore, iron is oxidized and removed at the upper part of filter vessel; manganese at the lower part of filter bed.

From this respect, too, if filtration is to be done with only one vessel, it is necessary to take a large layer thickness. When raw water contains large quantity of iron and manganese, or in the case of treating water with iron and manganese not readily oxidized, it is recommended to install two filter vessels connected in series, eliminating iron through the first vessel and removing the remaining iron and manganese through the second vessel.

As to filter media to be employed, it is effective to use Toyolex F in the first vessel and Ferrolite MC in the second vessel.



3. Outline of Manufacture

1. Matrix

(1) Porous Ceramics

We are using the porous ceramics media obtained through our many years' research for matrices which are fitting to three conditions of

- ① being rich in porosity.
- ② being excellent in adherent property against the film.
- ③ being physically and chemically stable as filter media.

(2) Selected Sand

The sand selected for the matrix of Manganese Sand is quality silica sand having a large silicon content produced at Awaji Island in Hyogo Pref. and Kashima in Ibaragi Pref., which is widely used in such treatments for city water and large-scale industrial water.

Table 1. Chemical Composition of Matrices (Weight%)

Kind \ Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	Ig.loss	Use
Ceramics M	71.3	19.0	1.4	1.3	0.37	3.7	2.7	0.23	Ferrolite MC
Ceramics G	73.9	19.3	2.1	0.3	0.18	2.2	1.9	0.12	Toyolex F Ferrolite GC
Filter Sand (Awaji)	93.15	5.11	0.24	0.43	0.71	—	—	0.36	Manganese Sand
Filter Sand (Kashima)	92.18	6.26	0.31	0.39	0.66	—	—	0.2	Manganese Sand

2. Ferrolite MC, GC and SC and Manganese Sand

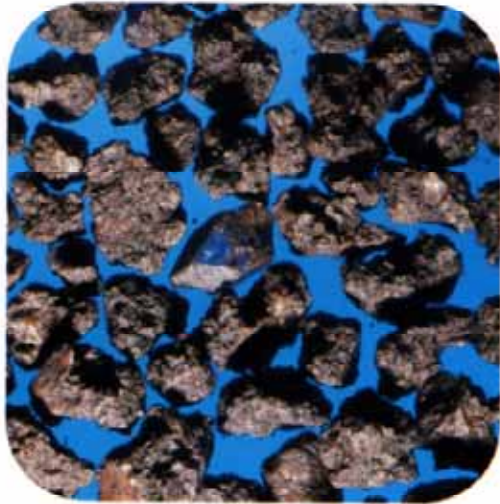
The matrices are reacted with manganese (II) chloride (MnCl₂·4H₂O) and potassium permanganate (KMnO₄) using a special catalyst in a rotary reaction kiln. In this process, viscous, dark brown, γ-type superior-quality manganese oxides with special crystal structure are produced. This film is coated to the matrices and then sintered to finish products.

3. Toyolex F

Taking Ceramics G as a matrix, iron hydroxide [Fe(OH)₂] is yielded. Using oxygen and a certain kind of catalyst, it is made into oxy-hydrated iron with special crystal structure, which is coated to the matrix.



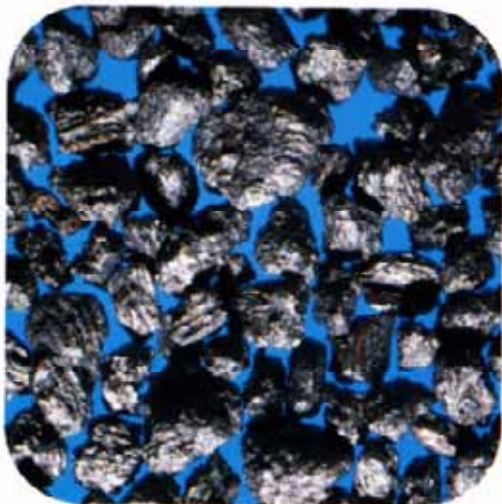
CATALYTIC OXIDATION FILTER MEDIA



FERROLITE MC



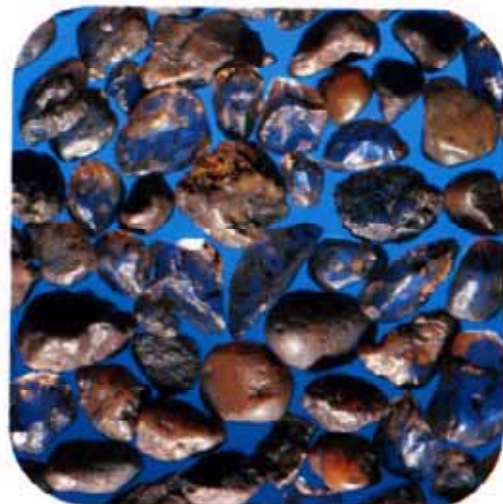
FERROLITE GC



FERROLITE SC



TOYOLEX F



MANGANESE SAND

1. Introduction

There are many cases where the underground water contains iron and manganese owing to the geological environment. The water containing iron and manganese causes various problems when used as water for all industrial fields, not to speak of drinking water and city water. So the elimination of iron and manganese from the water is essential.

Based upon our 25 years of experiences and technology we have had as a top maker of filter media for water treatment, our company have developed the catalytic oxidation filter media for iron and manganese removal (Ferrolite MC, Ferrolite GC, Ferrolite SC, Toyolex F and Manganese Sand). We shall introduce the outline of these filter media.

2. Features of Catalytic Type Oxidation Filter Media for Iron and Manganese Removal

- 1) Activation of filter media required at trial operation can be done very easily and in a short time.
- 2) Compared with the conventional deferrizing and demanganatizing filter media, washing time at trial operation can be largely reduced.
- 3) Deferrizing and demanganatizing capacity has been considerably improved. As to removal of manganese in particular, while the administrative water standard prescribes that manganese content should be 0.05 mg/ℓ or less, far less content can be achieved through these media.
- 4) Except for special occasions, precipitation vessel and aeration vessels are not necessary. Treated water of high quality can be obtained by applying raw water to these media directly from the well.
- 5) Treatment can be done at a water run speed of L.V. 10~30m/Hr, which is more than twice as fast as ordinary filtration.
- 6) Coagulants are not used except for special occasions, resulting in a low running cost.
- 7) Only periodic washing is required: periodic regeneration with chemicals is not required.
- 8) Humic chromaticity which has been difficult to remove in the past can be removed through these media without pretreatment.

