Formalin Purification

(Extracted from the Diaion Manuals pages 249 to 251)

12. Formalin Purification

Formaldehyde is manufactured by oxidation of the mixture of vaporized methanol with air catalyzed by silver metal or a mixture of an iron oxide with vanadium at around 600 °C:

$$2CH_3OH + O_2 \rightarrow 2HCHO + 2H_2O$$

Formalin is an aqueous solution of formaldehyde that adsorbs the reaction products and thus it includes impurities such as formic acid of 50 ~500 mg/l, a byproduct, and small amounts of metal ion dissolved from metal catalysts and facility materials. The reaction shceme to form formic acid is not yet clear, but it is thought to be two-step reaction of oxidation with a Cannizzaro's reaciton.

$$2HCHO + O_2 \rightarrow 2HCOOH$$

$$2HCHO + H_2O \rightarrow HCOOH + CH_3OH$$: Cannizzaro's reaction

Since formalin is unstable against alkalis and thermally, it is added with 4 ~13% methanol, as a stabilizer to form $CH_2(OH)OCH_3$, to prevent formic acid formation and precipitation of paraformaldehyde, hydrated polymer of formaldehyde.

Traditional formalin, around 40% concentration, is widely used as a raw material to produce fungicides, agrochemicals, synthetic resins and other organic compounds. In recent years, the demand for formalin has been diversified and thus the highly concentrated one, ≥50%, the non-methanol grade with 0 ~1% methanol and low methanol grade are on the market. Some products need to be highly purified, the amount of impurities are limited. IERs are applied for those purposes.

The purification methods with IERs are as follows:

1) AERs only

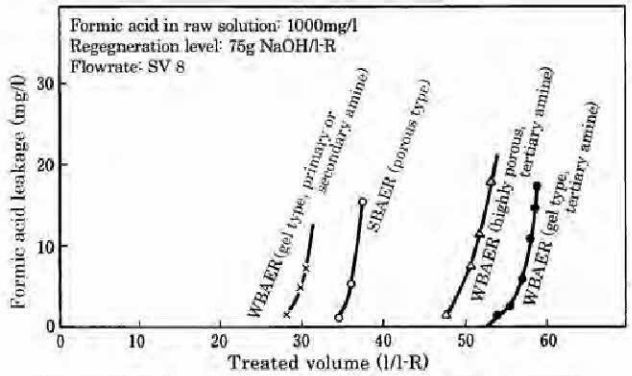
2) CERs and then AERs

3) CERs, AERs and mixed bed system

The simplest method 1) that can remove formic acid only is applied for the moderate needs. The method 2) is for the cases where metal ions should be eliminated and is commonly applied for general fields. The last method 3) is for highly purified needs.

Regarding regeneration of method 2), cocurrent regeneration is generally used. The countercurrent regeneration is, in SACERs particularly, recommended, from the point of the quality and effectiveness not only from saving of rinse waters and regenerants. (*Please see the chapter of Water Treatments.*)

SACERs with chemical and physical stabilities are recommended as CERs for purification of formalin.



[Fig.VII-12-1] Formic acid removal with several kinds of AERs

As for AERs, WBAERs with tertiary amines as functional groups, e.g. DIAION® WA10 and WA30, are applied for these purposes, because SBAERs have too strong basicity to promote excessive formation of formic acid by Cannizzaro's reaction and WBAERs with primary or secondary amines tend to form Shiff's bases with formaldehyde and to decrease their own exchange capacities. Fig.VII-12-1 summarizes removals of formic acid with these AERs.

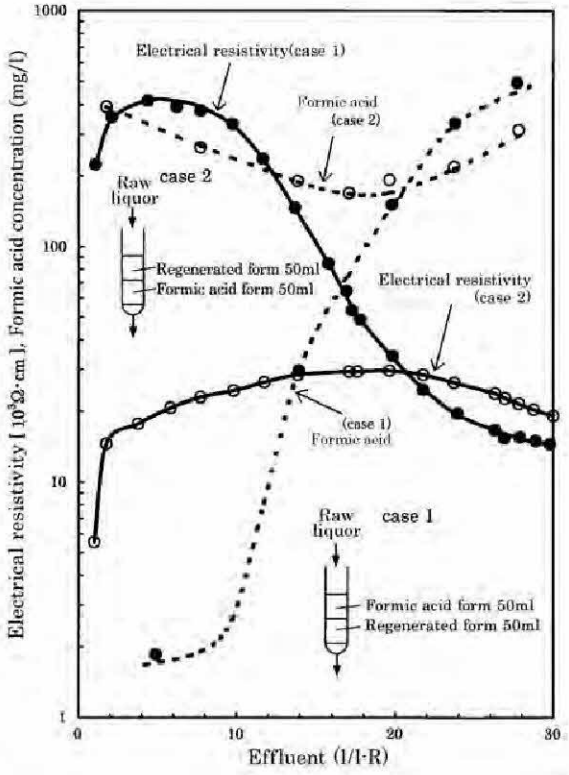
WBAERs are lower efficiency to be rinsed after regeneration with alkali than SBAERs. A small amount of alkali that remains within resin-particles or resin towers gradually elute into pure formalin of the next treatment and it might generate sodium formate by the reaction with formic acid which remains after the treatment with AERs and/or is generated at the contact with AERs. The pH of the purified formalin liquids is neutral and it does not notify the leakage of formic acid, and thus one should be careful about this. Formalin can be highly purified after recycling of the treated liquors at the beginning particularly.

The AERs used for highly purified formalin should be selected from the following points of view. The first point is whether it can be rinsed easily and sufficiently or not, since such easiness and efficiency is quite different among AER grades even with the same functional groups.

WBAERs have high selectivity to OH ions and thus formic-acid- form WBAERs are easily hydrolyzed. Formic-acid-form WBAERs which remain at the bottom of IER towers and are un-regenerated at the low regeneration level are hydrolyzed to cause the leakage of formic acid and to worsen the quality of product formalin. Thus, the regeneration level of WBAERs should be properly high. Hydrolysis of formic acid in formalin

purification is illustrated in Fig.VII-12-2.

Not only selection of suitable grade IERs but also designing of proper operation conditions, e.g. easiness or handling during rinse, prevention method against precipitation of paraformaldehyde, are very important in formalin purification with IERs.



[Fig.VII-12-2] Hydrolysis of formic-acid-form IERs