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Fouling of ion exchange resin of DM plant by hydrochloric acid from organic source

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To get consistent and expected results from the DM plant, it is important to maintain the resins in good condition and in a suitable environment. During the ion exchange process, water is passed through a resin bed and certain ions, depending upon the nature of the resin, are removed. Since the resin has only a certain capacity to exchange, it needs regeneration, once exhausted. The exhausted cation resin is regenerated by hydrochloric acid (HCl) and the anion resin by sodium hydroxide solution. Depending on the water quality, ion exchange resins may get fouled in different ways, resulting in loss of resin efficiency to deliver pure water. The present paper discusses some typical problems of fouling of cation and anion resin by hydrochloric acid, which is obtained from an organic chemical manufacturer. This type of fouling is not mentioned in any available literature.

Keyword: Hydrochloric acid, organic source, ion exchange resin, fouling

1. Introduction

Water used in power plants and other industries, needs moderate to severe treatment, depending on its quality [1]. Demineralised water of high quality is required for a high pressure boiler. Ion exchange resins are the heart of every demineralization (DM) or deionisation plant. To get consistent and expected results from the DM plant, it is important to maintain the resins in good condition in a suitable environment. During the ion exchange process, water is passed through a resin bed and certain ions, depending upon the nature of the resin, are removed. Since the resin has only a certain capacity to exchange, it needs regeneration, once exhausted. The exhausted cation resin, in hydrogen form, is regenerated by hydrochloric acid (HCl) and the anion resin by sodium hydroxide solution. Depending on the water quality, ion exchange resins may get fouled in different ways, resulting in loss of resin efficiency to deliver pure water. Resin fouling comprises adsorption of foreign matter, resulting in impairment of resin performance. Common forms include corrosion products, organic acids, bacteria, iron, turbidity in source water and oil [1, 4]. Resin fouling will result in capacity and quality reduction above and beyond the losses expected from typical degradation rates. [2] According to a reputed resin manufacturer of India (Ion Exchange India Ltd.), cation resin fouling occurs due to Iron and heavy metal fouling. In some cases, excessive use of aluminium sulphates in the pretreatment plant causes fouling of the cation resins. Excessive use of polyelectrolytes (which are high molecular weight organic substances) can cause irreversible fouling of the cation/anion resins [5]. Organic acids such as fulvic and humic acids formed by the decomposition of vegetable matter in the water can get adsorbed on anion exchange resins. Presence of oil in water can also cause physical fouling of the resin surface.

The present paper discusses some typical problems of fouling of cation and anion resin by hydrochloric acid, which is obtained from an organic chemical manufacturer. Since the cation resin was fouled, the output decreased and the rubber line of acid got removed resulting in a puncher.

1.1 Indian Standard IS 265:1993

According to Indian Standard, IS 265:1993, hydrochloric acid is classified under four grades depending upon the impurity content:-

1. Technical grade (Tech) 2) Chemical pure grade (CP) 3) Analytical reagent grade (AR), and 4) Boiler water grade (BW). Indian Standard is based on Hydrochloric acid obtained from inorganic industries such as the Chlor-alkali industries, which are usually the sole suppliers of hydrochloric acid. Indian standard for Hydrochloric acid obtained does not include from organic source.

1.2 Hydrochloric acid from Organic acid source

With the growth of various organic chemical producers after the 1990s, hydrochloric acid is generated as a byproduct in a number of organic chemical industries like the manufacturers of Chlorinated paraffin, Benzyl Chloride, Benzaldehyde, Benzotrichloride, Thionyl Chloride, Sulphuryl Chloride and Sulphur dichloride etc. Some of the chemical reactions are

shown below. Hydrochloric acid, thus produced undergoes refining processes to increase its purity of minimum 30%. Therefore the organic impurities are invariably present in some quantities. It is very difficult to detect at the customer end because of its variable nature.

1. Benzyl chloride

$C_6H_5CH_3+cl_2$ ----- $C_6H_5CH_2Cl + HCl$

2. Thionyl Chloride

$ROOH+SOCl_2$---------$ROCl+SO_2+HCl$

3. Benzyltrichloride

$C_6H_5CHCl_2+Cl_2$----------$C_6H_5CCl_3+HCl$

4. Chloroparaffin

$CnH_{2n+2} + Cl_2$ ---------- $CnH_{2n}+_2$-mclm +HCl

2. Material and Methods

2.1 Method developed for qualitative detection of organics in Hydrochloric acid

A simple method was developed in VIPL laboratory for qualitative detection of organics from different organic industry source. Hydrochloric acid was neutralized by an excess of Sodium Hydroxide, with the alkali addition being done very slowly, as the reaction is exothermic, The precipitate is allowed to cool at room temperature and then beaker is kept under refrigeration for 20-30 minutes, if the organic content in acid is low then the precipitation is observed only after refrigeration . All the organics show white precipitate in alkaline condition as shown in fig 1.

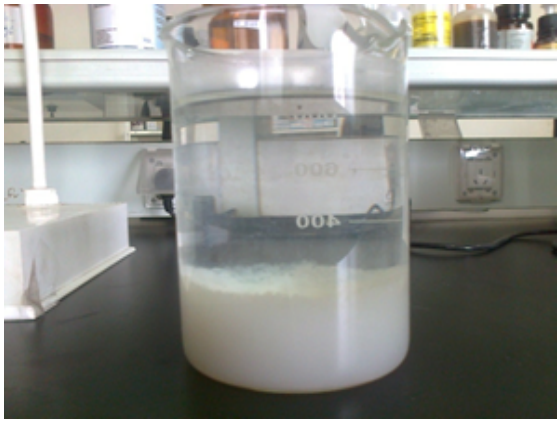

Fig 1: Organic matter precipitated in alkaline condition.

3. Results and Discussion

a) Impact on Ion-exchange Resins and cost benefit analysis

30% fall in cation exchanger output was observed and frothing was observed every time during regeneration. Frequent regeneration failure due to bed compactness and slimy layer formation over resin. Organics which is present in Hydrochloric acid becomes undetected as it is soluble in hydrochloric acid and causes physical fouling of the resin surface. Laboratory test shows that frothing is more in Hydrochloric acid concentration of 10% and more white precipitates observed after rinsing of cation resin with long term soaking of resin with acid. This proves that the organics are more soluble concentrated acids. It may be presumed that organics can cause irreversible fouling of the cation resins; slowly it gets carried over to anion exchanger where it also causes fouling. According to Sanemasa uptakes of benzene and 1,2 alkylbenzenes (from toluene to n-pentylbenzene including xylene and trimethylbenzene isomers) by both strong acid cation (Dowex 50W-X4 and X8) and strong base anion (Dowex 1-X4 and X8) exchange resins have been studied in aqueous solutions at 25 ^{0}C and the resin affinity for solutes has been analyzed. The K values of benzene and alkyl benzenes were larger than the K values of aliphatic hydrocarbons expected from the K values [6].

The cost analysis is as under.

1. Cost of Hydrochloric acid from organic source is Rs 2000/- per ton
2. Cost of Hydrochloric acid from chloralkali source is Rs 3400/ per ton
3. Cost of Cation resin is Rs 81/litre and anion resin is Rs 195 /litre therefore average Qty of cation resin is 9000 ltrs and anion is 13500 ltrs.
4. Total Average cost of cation and anion resin is 729000 +2632500 =33,61500 /- per year or in two year.
5. As the organics will be carried with DM water, which ultimately affects the final DM water quality.

Hydrochloric Acid used from Chlor- Alkali source	Hydrochloric Acid used from Organic source
1. Cost of hydrochloric acid is Rs 3500/ MT average @22 MT of acid /month = Rs 9,24000/- yearly	1. Cost of hydrochloric acid is 2000/MT,528000/- yearly+ 30% =15,8400 = 6,86,400 yearly
2. Total cost - Rs 9,24000/- approx.	2. Cost of Cation Resin is Rs 81/litres,and anion resin is Rs 195/litre . Total quantity of cation resin is 9000 litres and anion resin 13500 litres.
3. Life of resin is minimum 10 years with 5% top up every year. Cost – Rs 1,68,075/- per year	3. Cost of resin is Rs. 33,61,500/- per two year i.e Rs 16,80,750/year.
	4. Cost of pipline and maintenance cost 2 lakh per year approx.
Total cost – Rs 10,92,075/- Per year	Total cost Rs 25,67,150/- Per year

b) Corrective action taken to prevent hydrochloric acid from Organic source

1. Appraised the management and Purchase department regarding the problem at DM plant due to Hydrochloric acid from organic industry source.
2. Vendor shortlisted on the basis of acid supplier from choralkali sources only same is incorporated in our Technical evaluation report. Confirmation of Chloralkali source is done on the basis of original excise documents and laboratory analysis.

3. Additional analysis for organic content is carried out by neutralization method.

4. Conclusion

From the study it is concluded that Hydrochloric acid from organic industries is detrimental for the ion exchange process even if it is present in minute levels. Though hydrochloric acid from organic sources appears to be the cheaper option, but it will prove very costly in the long run. Detection method as developed in VIPL lab is simple and can be performed without any specialized instrument. This type of fouling is not mentioned in any available literature, not experienced by any resin manufacturer and not mentioned even in IS standard, therefore its first kind of innovative work done in our VIPL lab.

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