

# **EFFECT OF WATER CHARACTERISTICS, METHOD OF CATION EXCHANGE RESINS MODIFICATION WITH FERROUS COMPOUNDS ON THE EFFICIENCY OF DISSOLVED OXYGEN REMOVAL**

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## **ABSTRACT**

In Ukraine the biggest volumes of water in industry are used for the refrigerating systems. The transition to a closed water circulation systems can minimize wastewater discharge into natural water bodies. This can be achieved with new methods of stabilizing water treatment that prevent scale formation and corrosion.

A corrosion and destruction of heat exchangers elements and pipelines of the industrial plants result in considerable expenditure of energy and materials and lead to water contamination. Thus, during operation of these plants considerable attention is devoted to the water chemical regime, one indicator of which is low oxygen content.

The removal of dissolved oxygen (DO) from water was studied experimentally in cation-exchange resins modified by ferrous compounds.

The influence of ion-exchange resin form on the reducing ability and secondary contamination of water with iron ions was studied. The results show that reducing ability increases with a decrease in reaction medium at low water hardness and sorption of ferrous ions occurs efficiently on strong-acid cation exchange resin in the acid form. The exchange capacity of sodium-based ion exchangers grows with the acidification of ferrous sulfate solutions to the concentration of the sulfuric acid up to 1.5%. The best results with multiple processing of ion exchange resins with ferrous solutions were obtained using macroporous sorbents.

**KEYWORDS:** oxygen, oxidation-reduction ion exchange resin , sorption, iron, capacity

## **INTRODUCTION**

Nowadays, the main problem in industrial, power plant, municipal engineering water consumption is transition to the closed water circulating systems.

The transition to a closed water circulating systems can minimize wastewater discharge into natural water bodies. This can be achieved with new methods of stabilizing water treatment that prevent scale formation and corrosion. Therefore water quality requirements rise.

Reliable operation of thermal power plants is ensured, first of all, by preventing corrosion of the structural materials in the equipment and piping. A corrosion and destruction of heat exchangers' elements and pipelines result in considerable expenditure of energy and materials and lead to the water contamination. In neutral aqueous medium in power plants corrosive processes are usually caused by the presence of dissolved oxygen (Kudinov et al., 2009).

The removal of DO from water can be achieved by either physical or chemical methods. The physical methods such as thermal degassing, vacuum degassing or nitrogen bubble de-aeration have inherent drawbacks in terms of both operating costs and bulky construction.

All of the known methods for deoxygenation that use soluble chemical reagents such as sodium sulfite, hydrazine, formic acid, hydroquinone, diethylhydroxylamine, etc involve a change in the composition of the water medium, which is not always acceptable. These methods also have a range of technological limitations, including: a dependence on the presence of a catalyst e.g. metal oxides, the toxicity of most of the reagents used, the influence of the temperature and pH value of the medium on the rate at which the reagent reacts with oxygen, the undesirable presence of suspended solid particles in the end product, etc.

Methods for removal of oxygen from water using polymer materials are currently under development. The oxidation-reduction method is based on the usage of redox ion exchange materials — high molecular compounds capable of reverse oxidation-reduction conversion in the solutions of oxidation-reduction systems. In the redox ion exchange resins the oxidation or reduction function is performed by mobile ions in ion exchange resins bound to the polymer material by immobile, fixed ions by ionic or coordination bonds. During the reaction, redox ion exchange resins are not dissolved and their phase state does not change and this is their primary advantage over soluble redox agents. Another important advantage of the redox ion exchangers is the possibility of repeated use. After exhaustion of the redox capacity, the materials are converted into their original form by a reducing agent or an oxidant. The technical process of oxygen removal reduces to simple filtration of the water through a column full of a granular ion exchange reducing agent, with periodic chemical regeneration of the agent as its reducing capacity is exhausted. The required degree of oxygen removal is achieved through appropriate choice of the redox material, its fractional composition, the column height, and the flow rate of the water (Kravchenko et al., 1982).

## **MATERIALS AND METHODS**

While making and using oxidation-reduction ion exchangers problems associated with the processes of modification of ion exchange resins, assessing their quality, reduction capacity, reliability and duration of use appear. The aim of this study was to evaluate the effects of conditions of modification cation exchange resin with iron (II) compounds, to study influence of water characteristics on the efficiency of water deoxygenation, to explore reduction capacity of obtained oxidation-reduction ion exchange resins

During the studies such cation exchange resins as CU-2-8, macroporous Amberlite 252H, Purolite C150, Dowex MSC 1H, as well as weak-acid cation exchange resin Dowex MAC-3 were used.

To obtain Fe<sup>2+</sup>-based cation exchanger the solution of ferrous sulfate (II) at a concentration of iron (II) ions from 125 to 1079 meq/L was filtered through the resin bed (volume of resin 10, 20 or 50 cm<sup>3</sup>) at a rate of 1.5 cm<sup>3</sup>/min. Na<sup>+</sup> and H<sup>+</sup>-based cation exchangers were used. H<sup>+</sup>-based cation exchanger was obtained by infiltration of 5% hydrochloric acid through the column full of cation exchange resin, while in order to get Na<sup>+</sup>-based one the 2% solution of NaOH was used.

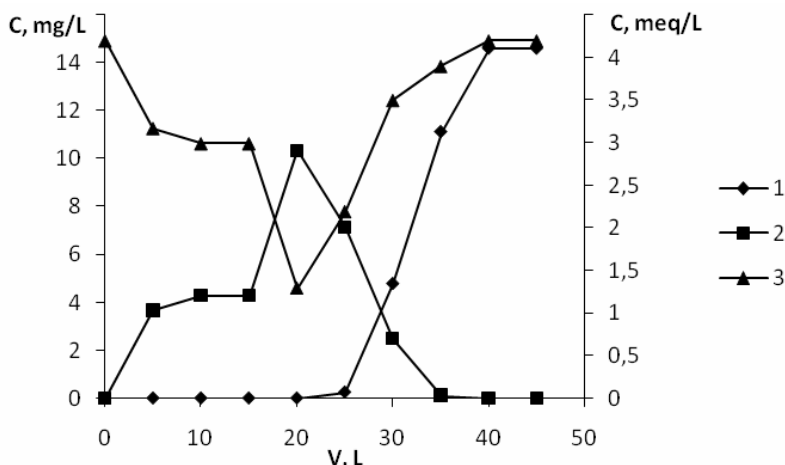
When processing the Fe<sup>2+</sup>-based resin with 2% alkali solution cation exchanger turns into Na<sup>+</sup>-based with Fe(OH)<sub>2</sub> located in the pores. For the sorption of ferrous ions on the strong acid cation exchanger the solution of ferrous sulfate was used (C<sub>Fe<sup>2+</sup></sub> = 720 meq/L) that contained sulfuric acid at a concentration of 0.5-2.0%.

To evaluate the reduction capacity (capacity for oxygen or other oxidants, such as NaClO<sub>3</sub>, in meq/L) tap water, sodium cycled water or NaClO<sub>3</sub> solutions were infiltrated through the cation exchange resins modified with ferrous compounds. Water flow rate was 15-20 cm<sup>3</sup>/min and

for NaClO<sub>3</sub> solutions it was 5 cm<sup>3</sup>/min. Control of water hardness, dissolved oxygen, iron, free chlorine was carried on using well-known techniques (Lurje et al., 1974, Kulskii et al., 1980).

## RESULTS AND DISCUSSION

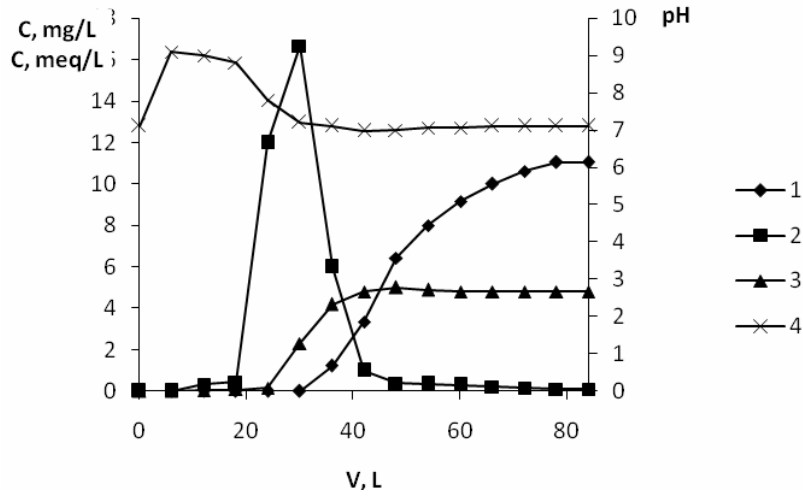
Reduction capacity of redox ion exchangers depends on the amount of sorbed iron ions, chemical form of the resin and water characteristics. According to the charts (Fig.1 and 2), reducing capacity grows during the transition from the Fe<sup>2+</sup>-based cation exchanger CU-2-8 (Fig. 1) to Na<sup>+</sup>-based cation exchanger with Fe(OH)<sub>2</sub> located in pores (Fig. 2).



**Figure 1.** Dependence of concentration of DO(1), iron ions(2) and ions of water hardness(3) on the amount of infiltrated water ( $W.H_{initial}=4.2$  meq/L,  $C_{O_2 initial}=14.6$  mg/L) through Fe<sup>2+</sup>-based CU-2-8 ( $V_{ionite}=50$  ml, Capacity for Fe<sup>2+</sup>=2.978 eq/L, Capacity for O<sub>2</sub>=1.08 eq/L)

While infiltrating the tap water with a hardness of 4.2 meq/L there is a significant washout of iron ions from the resin as a result of the irdisplacement with water hardness ions, which leads to a decrease in DO exchange capacity of the resin.

Iron ions are washed out less from the ferrous hydroxide due to the low solubility of the latter though their concentration in water reaches 2.8mg/l (Fig. 2). Obviously the reason of this is pH value of medium.

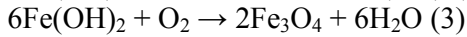
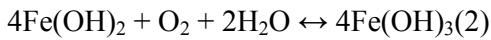


**Figure 2.** Dependence of concentration of DO (1), iron ions (2), ion of water hardness (3) and pH value (4) on the amount of infiltrated water ( $W.H_{initial}=4.8\text{ meq/L}$ ,  $C_{O_2 initial}=11.04\text{ mg/L}$ ) through  $\text{Na}^+$ -based CU-2 -8 with  $\text{Fe}(\text{OH})_2$  located in pores ( $V_{ionit}=50\text{ ml}$ , Capacity for  $\text{Fe}^{2+}=2.96\text{ eq/L}$ , Capacity for  $\text{O}_2=1.352\text{ eq/L}$ )

Obviously, pH value increases because of the  $\text{Na}^+$ -based redox ion exchanger that can exchange sodium ions for the ions of water hardness. The reaction that leads to alkalization

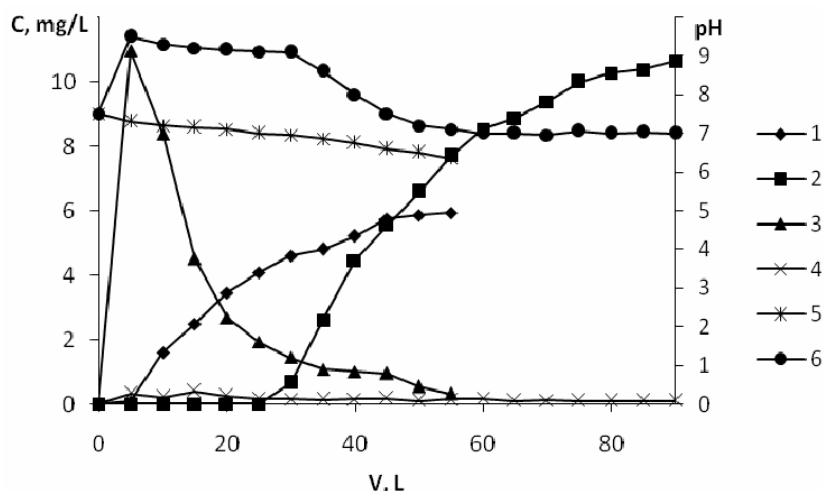
$$2\text{KtNa}^+ + \text{Me}(\text{HCO}_3)_2 \rightarrow \text{Kt}_2\text{Me}^{2+} + 2\text{NaHCO}_3(1)$$

Formation of sodium bicarbonate causes alkalization of the water and pH rise (Gomelya et al., 2008). Thereby at this stage at  $\text{pH} \approx 9$ , when the solubility of  $\text{Fe}^{2+}$  in the water is low, iron ions are virtually absent. It was assumed that oxidation process may proceed by formation of ferrous hydroxide or ferrite



According to the first reaction, 2 meq of ferrous ions are needed for reduction of 1 meq of  $\text{O}_2$ . As for the second, 3 meq of ferrous ions reduce 1 meq of  $\text{O}_2$ .

While the sodium cycled water (Fig. 3) run through the  $\text{Na}^+$ -based redox ion exchanger with  $\text{Fe}(\text{OH})_2$  located in pores, almost no iron ions leach due to higher pH values ( $\text{pH} \approx 8,5-9,6$ ) (Gomelya et. Al., 2008). However, the capacity for oxygen is less than during filtration of tap water. The reason is that at  $\text{pH} > 9$  the formation of ferrite occurs.



**Figure 3.** Dependence of concentration of DO (1, 2), iron ions (3, 4), and pH value (5, 6) on the amount of infiltrated sodium cycled water ( $W.H_{initial}=0.7$  meq/L,  $C_{O_2 initial}=10.64$  mg/L, Alkalinity=6.6 meq/L, pH=7.5) through  $Fe^{2+}$ -based CU-2 -8 ( $V_{ionit}=50$  ml, Capacity for  $Fe^{2+}=2.9$  eq/L, Capacity for  $O_2=0.889$  eq/L) (1; 3; 5) and  $Na^+$ -based with  $Fe(OH)_2$  located in pores ( $V_{ionit}=50$  ml, Capacity for  $Fe^{2+}=3.1$  eq/L, Capacity for  $O_2=1.187$  eq/L) (2; 4; 6)

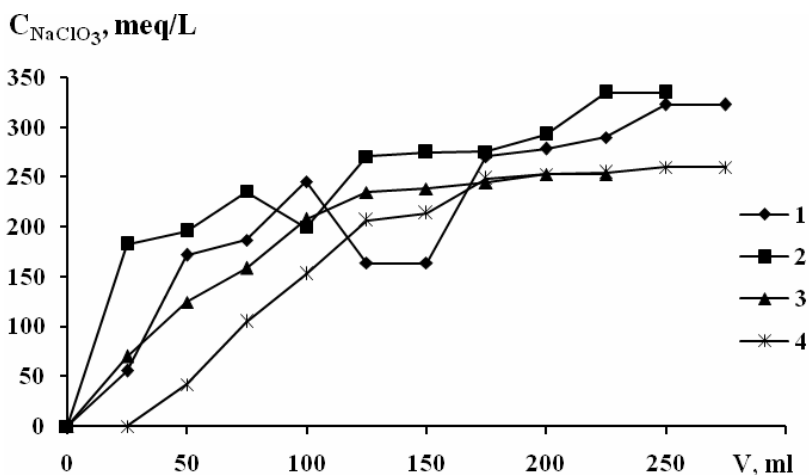
In addition to the mechanism of oxidation of iron the capacity for oxygen of the redoxide ionites is undoubtedly affected by its capacity for iron.

On the basis of that statement the usage of high concentrated solution of ferrous sulfate during the sorption on the cation exchanger in acid form leads to the acidification of the solution that reduces the sorption capacity of the cation exchanger. Thus, it can be assumed that a greater exchange capacity cation exchange resin has in a salt form. These results were obtained during the sorption of zinc, cadmium and nickel (Gomelya et al., 1998). However, in this case the statement is valid only for weak acid cation exchanger. Strong acid cation exchangers in the acid form have a higher capacity for iron compared to the sodium form. Moreover, the capacity of the cation exchanger CU-2-8 in the sodium form increases from 1660 meq/L when using  $FeSO_4$  solution without acidification up to 3510 meq/L at a concentration of sulfuric acid 1,5% in the solution of  $FeSO_4$ . At 2% solution of sulfuric acid capacity of the resin for iron (II) reached 3420 meq/L. This happens because iron ions form associations such as  $FeX_2^+ \leftrightarrow Fe_2^{2+}[FeX_6]^{4+}$  (Gomelya and Tereschenko, 1998) in acidic medium. Therefore, the adsorption rate for iron (II) compounds increases in weak and medium acid solution at a concentration of free sulfuric acid up to 20g/L. It should be noted that weak-acid cation exchange resin Dowex MAC-3 had the greater iron capacity even in  $Na^+$ -form.

Very difficult task is the regeneration of redox ion exchangers. As it was shown earlier, the use of the cation exchange resin in the  $Fe^{2+}$ -form is impossible because of water contamination with iron. Reduction of  $Fe(OH)_3$  or  $Fe_3O_4$  which are formed in the pores of the resin after oxidation of  $Fe(OH)_2$  is very difficult. Simpler agents such as sodium bisulfite in a weak acid medium don't reduce iron (III). The use of more expensive agents is impractical. Therefore, the best way is re-sorption of iron (II) ions on cation exchanger followed up by its hydrolysis. But, considering the accumulation of iron oxides and hydroxides in the pores that block the gel sections, repeated cycles of regeneration can not be large.

The changes of capacity for iron (II) for different cation exchangers, their reducing ability on  $NaClO_3$  depending on the number of filtrations were studied. Since the evaluation of DO

reduction ability of oxidation-reduction ion exchanger is a very continuous process taking into account the low solubility of oxygen in the water, solutions of sodium chlorate at a concentration of 250-350 meq/L (Fig. 4) were used to determine the reducing capacity of the cation exchanger. As it can be seen from Fig. 6, the values of redox ion exchange resin capacity for oxidants in this case are close to those obtained by using water saturated with air (Fig. 1, 2, 3).



**Figure 4.** Dependence of  $\text{NaClO}_3$  residual concentration on the volume of solution with the initial concentration of 323 (1), 335 (2), 253 (3) и 260 (4) meq/L infiltrated through Amberlite 252 H (1) (Exchange capacity for  $\text{Fe}^{2+}=1.790$  eq/L, Capacity for  $\text{O}_2=0.88$  eq/L,  $V_{\text{ionite}}=20$  ml), Purolite C 150 (2) (Exchange capacity for  $\text{Fe}^{2+}=1,790$  eq/L, Capacity for  $\text{O}_2=0.88$  eq/L,  $V_{\text{ionite}}=20$  ml), Dowex MSC 1 H (3) (Exchange capacity for  $\text{Fe}^{2+}=1,24$  eq/L, Capacity for  $\text{O}_2=0.62$  eq/L,  $V_{\text{ionite}}=20$  ml), Dowex MAC-3 (4) (Exchange capacity for  $\text{Fe}^{2+}=4.15$  eq/L, Capacity for  $\text{O}_2=2.07$  eq/L,  $V_{\text{ionite}}=20$  ml), that where modified with  $\text{Fe}(\text{OH})_2$

Data on the ion exchangers capacity based on the number of filtrations are given in Table 1. In addition to the most affordable in the Ukraine cation exchange resin CU-2-8 macroporous cation exchangers Amberlite 252 H, Purolite C150, Dowex MSH 1H and weak-acid cation exchange resin Dowex MAC-3 were used.

It was assumed that accumulation of iron oxides and hydroxides in the pores less block gel areas of the resin and is less dependent on the number of filtration when using macroporous cation exchangers.

However, in almost all cases, decrease in reduction capacity was observed while the number of filtration increased. At the same time cation exchanger CU-2-8 in the range of strongly acid cation exchangers was characterized by higher capacity for all cycles of filtration, and weak-acid cation exchange resin Dowex MAC-3 had the highest capacity for sorption of iron on the first and second filtration cycle. On the third filter cycle its capacity dropped significantly, however, after the cavitation processing on the fourth filtration cycle it increased 2.5 times.

**Table 1.** Effect of number of filter cycles on the ferrous ions sorption from the 10% solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  by cation exchange resins

№	Cation exchanger	Number of filter cycles	Cation exchange form	Capacity, $\text{Fe}^{2+}$ , meq/L	C $\text{NaClO}_3$ , meq/L		Capacity, $\text{O}_2$ , meq/L
					Initial	Final	
1	CU-2-8	1	$\text{H}^+$	3,03	313,0	187	1,260
2		2	$\text{Na}^+$	2,14	290,0	203,1	0,865
3		3	$\text{Na}^+$	2,90	310,0	184,0	1,260
4		4	$\text{Na}^+$	1,60	395,0	320,0	0,750
5		5	$\text{Na}^+$	1,25	423,0	372,1	0,510
6	Amberlite 252 H	1	$\text{H}^+$	2,62	315,0	203,6	1,114
7		2	$\text{Na}^+$	2,12	310,0	221,	0,883
8		3	$\text{Na}^+$	1,72	295,0	220,5	0,745
9		4	$\text{Na}^+$	1,23	300,0	246,5	0,535
10		5	$\text{Na}^+$	0,96	310,0	267,0	0,430
11		6	$\text{Na}^+$	0,61	320,0	294,1	0,259
12	Purolite C 150	1	$\text{H}^+$	1,50	315,0	249,8	0,652
13		2	$\text{Na}^+$	0,76	310,0	277,0	0,330
14		3	$\text{Na}^+$	0,56	300,0	258,3	0,417
15		4	$\text{Na}^+$	0,85	300,0	264,1	0,359
16		5	$\text{Na}^+$	0,54	295,1	271,6	0,235
17		6	$\text{Na}^+$	0,51	325,2	303,3	0,219
18	Dowex MSC 1 H	1	$\text{H}^+$	1,92	340,0	256,8	0,835
19		2	$\text{Na}^+$	1,91	321,0	239,4	0,816
20		3	$\text{Na}^+$	1,34	310,1	252,6	0,575
21		4	$\text{Na}^+$	1,24	300,0	28,3	0,517
22		5	$\text{Na}^+$	0,94	305,2	264,7	0,405
23		6	$\text{Na}^+$	0,74	310,0	278,2	0,318
24	Dowex MAC-3	1	$\text{Na}^+$	4,56	310,0	103	2,070
25		2	$\text{Na}^+$	2,9	336	194	1,420
26		3	$\text{Na}^+$	1,1	253	200	0,530
27		4	$\text{Na}^+$	2,54*	231	106	1,250

\*after cavitation processing

## CONCLUSIONS

On the basis of the presented results it can be stated that tap water deoxygenation with  $\text{Fe}^{2+}$ -based CU-2-8 leads to contamination of water with iron ions due to their displacement from the resin with ions of water hardness thus it causes a significant decrease in reduction ability up to 30% or more. The process of sodium cycled water deoxygenation runs more effectively on the cation exchanger modified with  $\text{Fe}(\text{OH})_2$  rather than one  $\text{Fe}^{2+}$ -based.

At high pH the oxidation process of iron on the cation exchanger runs simultaneously with the formation of ferrite  $\text{Fe}_3\text{O}_4$ , which 1.5 times reduces the capacity for DO reduction. The capacity for  $\text{Fe}^{2+}$  ions on the strongly acid cation exchange resins rises with increasing in concentration of sulfuric acid in a solution of ferrous sulfate up to 1.5%.

The effect of the number of filtration cycles on the efficiency of regeneration of oxidation-reduction ion exchange resin was determined. It was shown that the capacity of macroporous cation exchange resins for the  $\text{Fe}^{2+}$  ions coarsely falls 2-3 times after 6 filter cycles, for the CU-2-8 it decreases after 5 filter cycles, for weakly acid cation exchanger Dowex MAC-3 it drops after 3 filtration cycles.

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