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ELIMINATION OF CORROSIVITY OF NATURAL WATER BY SIMULTANEOUS REMOVAL OF OXYGEN AND MINERAL SALTS BY ION EXCHANGERS ¶

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ABSTRACT

Corrosivity of natural water controls concentration of soluble oxygen and amount of mineral salts. In order to decrease the corrosivity of water are applied deoxygenation and demineralization methods. This article presents investigations on oxygen and mineral salts removal by ion exchangers. A special kind of a bed which contained two ionic forms : sulphite and hydroxyl was investigated for simultaneous removal of oxygen and anions from water. The natural water from a deep well supplied the bed after its initial decationization on strong acid cation exchanger. The model solutions were used with hydrochloric and sulphuric acids in amounts equal to decationization of water from the well, too.

It was stated that the removal efficiency of oxygen and anions was very high. The bed may be used as a difunctional ionic column for the simultaneos removal of oxygen and anions if demineralization process is designed by ion exchanger's method. The corrosivity of water may be eliminated and technological installation should be simplificied using such a bed.
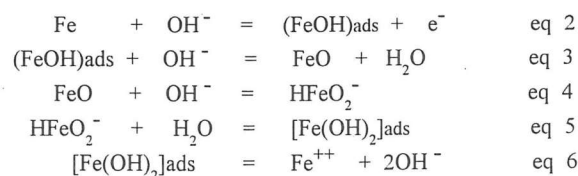
INTRODUCTION

In oxygenated natural water, its corrosivity depends on electrochemical processes resulted with soluble oxygen and mineral salts. Oxygen causes cathodic reaction which potential is more than 1 volt greater than hydrogen electrode and may be presented as a equilibrium potential which depends on : the concentration of OH^- ions and the partial oxygen pressure pO_2 .

$$E' = E^0 - RT/F \ln(OH^-) + RT/4F \ln pO_2 \quad [1] :$$

$$O_2 + 2H_2O + 4e^- = 4OH^- \qquad \text{eq 1}$$

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Oxygen controls also corrosion by production of hydroxyl ions that takes role in most reactions, see equations 2 - 6. The oxidative layer generated on the surface of iron is low protective against the oxygen diffuse and the product (FeOH)ads , initially adsorbed , is removed in consequence of the multistage reactions , eqs. 2 - 6. The slowest step , eq 3 , is markedly fasted by hydroxyl ions formed from eq 1 [2 , 3] :

$$Fe + OH^- = (FeOH)ads + e^- \qquad eq\ 2$$
$$(FeOH)ads + OH^- = FeO + H_2O \qquad eq\ 3$$
$$FeO + OH^- = HFeO_2^- \qquad eq\ 4$$
$$HFeO_2^- + H_2O = [Fe(OH)_2]ads \qquad eq\ 5$$
$$[Fe(OH)_2]ads = Fe^{++} + 2OH^- \qquad eq\ 6$$

The influence of oxygen may be discussed in combination with different kinds of salts that are contained in natural water. It is known that chloride and sulphate ions are very aggressive acting individual specific effect as well as increasing of water electrical conductance [4]. The later controls electrochemical corrosion in the water environment, too.

Deoxygenation and demineralization of the natural water are often required for many industrial purposes. The treated water, depended on working parameters, must not exceed maximum of indices values [5, 6]. Concentrations of oxygen and mineral salts are the main indices which are limited in the treated water. The examples of the requirements are following :

Source	Indices				
	Oxygen	Conductance	pH	Hardness	CO_2
	mg/L	μS/cm 25^0C		meq/L	mg/L
Instruction -Feeding Water Quality Sosnowieckie Zakłady Budowy Kotłów Polish Producer of Boilers pressure 20 - 42 bar [5]	<0,02		7 - 9,5	<0,00357	<1
Steam generator feedwater Water Treatment Handbook Edited Degremont 1991 [6]	<0,005	3 - 13	9,0 - 9,2		

PROBLEM

Removing of the oxygen and the mineral salts cause elimination or the decrease of water corrosivity . Industrial processes of the water demineralization are well known and there are no problems from a technological view point. However, removal of oxygen from the water is still

being investigated and modified [7]. One can observe improvements in the processes of oxygen reduction using advanced reduction catalysts [8]. These methods are applied as the separate steps of the oxygen reduction from the water that was treated initially. If demineralization is made by the ion exchange processes, for instance , the technological installation consists of two steps of the treatment , namely cation and anion removals. Thus, the process of the water treatment together with deoxygenation process includes three steps. Sometimes, three steps system is not neccessary and then it is difficult to execute it . It might be used , for example , for installation with small capacity or system where thermal process cannot be applied.

That article presents the results of investigations upon a new method of oxygen removal with simultaneous demineralizing of water. As the basic process of the water treatment it assumed ion exchange in order to obtain its corrosivity elimination as the result of salts and oxygen removal. Strong basic anion exchanger was used in two layers - upper and lower - in a sulphite and hydroxyl forms , respectively. The column was fed with the water containing chloride and sulphate acids in the amount equal to values to the decationization process of natural water by strong cation exchanger. The water was saturated with oxygen. The removal efficiency of oxygen and anions in two layers bed and some operational parameters were determined. Some reactions are presented in the context of explanation of redox and ion exchange processes in the bed.

METHODS AND MATERIALS

Investigations were conducted in a laboratory scale equipment detailed in the earlier work [9]. . The apparatus consisted of the water supply system with flow meter and the ion exchanger's column with the special construction, and it was equipied with following meters : pH, the concentration of oxygen and the conductance. The measurements were made according to the Polish Standards [10]. At the same time it might be measured in the effluent concentration of residual oxygen by colorimetric indigo method, as well [11]. The later was used for determination up to value 100 μg/L O_2 in period before and after breakpoint.

Experiments were made during continuous flow of water feeding according to the ion exchange standard technic's for breakthrough curves determining.

The strong basic anion exchanger II type Wofatit SBK 0,3 L made in Germany was used in the column with a perforated bottom , of 28 mm diameter and 1 m high. Due to special construction of the column, regeneration of the bed in two the same volume 0,15 L ionic forms , upper - sulphite and lower - hydroxyl, was possible. The bed was regenerated by the solutions of 4 % natrium sulphite and 4 % natrium hydroxide in divided standarized flow operations through of each layer during 45 minutes and after that rinsing was made.

Cycles of ion exchange were made for each of investigated water and then the effluent was determined with assumed program.

As the supply waters were used the HCl solutions of conc. 1,1 meq/L and HCl + H_2SO_4 3,7 meq/L (1,1 + 2,6 meq/L, respectively) , and the natural water from the deep well after decationization on strong acid cation exchanger, too . The specific velocity of the water was 20 BV/h of water or flow rate 10 m/h. That water had 3,5 meq/L of the mineral acidity after decationization on the strong cation exchanger in the hydrogen form Wofatit KPS , made in Germany.

The breakpoints of the bed both oxygen and salinity were determined and all breakthrough curves were obtained.

Full characteristics of water deoxygenation and demineralization were made with measurement of indices required for evaluation of both processes running in two ionic form layers of the bed. The amounts of oxygen and anions which were removed by each of ionic form of the bed - sulphite and hydroxyl - were estimated. The values of utilization degree of total capacity were calculated from experimental findings among others they were applied basic indices of the process such a volume of deoxygenation and demineralization water. These values are presented in relation to the ionic form as well as to total capacity of the bed, the later named as "general".

RESULTS

The results are presented in Table 1 and Table2. They characterize both processes in the bed , deoxygenation and demineralization.

As we may see from Table 1 the efficiency of oxygen removal was very high because residual concentration of oxygen was zero and 0,025 mg/L for the model solutions with 1,1 meq/L HCl and 3,7 meq / L HCl plus H_2SO_4 , respectively. Very good effect of deoxygenation for water from the well was obtained since the trace amount of oxygen 5 ppb in the effluent had been stated , see Table 2. These findings in comparision with high degrees of acids removal were obtained for all supplied waters, pointed out on very good acting of two layers bed in the simultaneous treatment process. Volumes of treated water are different and they depend on the amount of acids contained in the water. It is obvious that at higher amount of acids volumes of treated water were lower.

Operation capacity was estimated in relation to each of the ionic forms of the bed. As we may see, assumption , that sulphite form removed only oxygen, gave decrease its percentage of utilization with the increase of acid amounts in the influent. For higher values of acids it was only ca 20 %. However, the same values for hydroxyl form were very high, better than 60 % or even above 70 and 80 % for the highest amount of acids. Endly, the general indices of utilization degree in relation to total capacity of all volumes of ion exchanger had average values in the range from ca 46 % to ca 61 % as amounts of acid decreasing.

Table 1. The results of oxygen and acids removal from the model solutions

Indices	Unit	HCl solution 1,1 meq/L		HCl + H_2SO_4 solution 3,7 meq/L (1,1 + 2,6)	
		Influent	Effluent	Influent	Effluent
Oxygen concentration	mg / L	7,68	0,000	7,36	0,025
Mineral acidity	meq / L	1,1	0,00	3,7	0,00
Conductance	µS / cm	500	4 - 6	1920	4,5 - 6,1
pH		2,95	7,5 - 8,5	2,4	8,1 - 8,3
Volume of treated water	Bed Volume B V cu m / cu m	300		100	
Utilization degree of total capacity in relation to form sulphite hydroxyl ion general	%	60,4 62,9 61,7		19,3 70,5 46,0	

DISCUSSION

Difunctional anion exchanger in sulphite and hydroxyl ion forms is capable to removal of oxygen and anions from waters that contained acid ions. Sulphite form basicaly removed soluble oxygen but that very high efficiency was probably caused by its combination with hydroxyl form. Anion exchange of chloride and sulphate ions was in hydroxyl form of the bed and the good effect of water deanionization was obtained. That effect was the same as in conventional demineralization process of water by ion exchangers.

The results obtained for the model solutions of acids were in good relation with the findings for natural water from the well. This good agreement corroborates presumption with the same mechanism of processes.
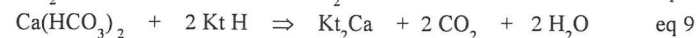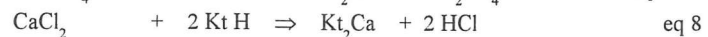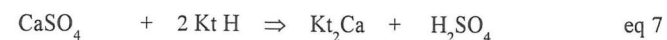
The lower values of utilization degree of total capacity of ion exchanger obtained in that experiments in comparision with other operation of water demineralizing may be explained as a result of "no opitimization" of reaction conditions in the applied bed. Optimization has to be done in the future, as well as funtions of ionic forms of the bed in chemical mechanism should be elucidated. In that time we may only roughly ilustrate processes in that difunctional bed. If it

Table 2. The results of oxygen and acids removal from the well water
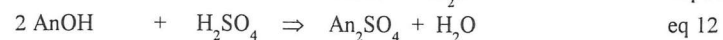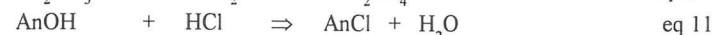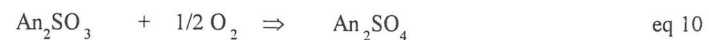after decationization and aeration

Indices	Unit	Influent	Effluent
Oxygen concentration	mg / L	7,36	0,005
Mineral acidivity	meq / L	3,5	0,00
Conductance	μS / cm	2100	2 - 6,2
pH		2,4	7,1 - 7,9
Volume of treated water	Bed Volume B V cu m / cu m		140
Utilization degree of total capacity in relation to form sulphite hydroxyl ion general	%		60,4 62,9 61,7

will be quoted with decationization processes of the natural water on strong acid cation exchanger, the summarized reactions are as following :

on strong cation exchanger in hydrogen form

$$CaSO_4 \ + \ 2\,KtH \ \Rightarrow \ Kt_2Ca \ + \ H_2SO_4 \qquad\qquad eq\ 7$$
$$CaCl_2 \ + \ 2\,KtH \ \Rightarrow \ Kt_2Ca \ + \ 2\,HCl \qquad\qquad eq\ 8$$
$$Ca(HCO_3)_2 \ + \ 2\,KtH \ \Rightarrow \ Kt_2Ca \ + \ 2\,CO_2 \ + \ 2\,H_2O \qquad eq\ 9$$

on difunctional bed

$$An_2SO_3 \ + \ 1/2\,O_2 \ \Rightarrow \ An_2SO_4 \qquad\qquad eq\ 10$$
$$AnOH \ + \ HCl \ \Rightarrow \ AnCl \ + \ H_2O \qquad\qquad eq\ 11$$
$$2\,AnOH \ + \ H_2SO_4 \ \Rightarrow \ An_2SO_4 \ + \ H_2O \qquad\qquad eq\ 12$$

Decationization reactions eq 7 - 9, are also with other cations contained in the natural water such as Na, K, Mg and the effluent contain the same mineral acids and soluble carbon dioxide,

finally. Desorption of carbon dioxide is made by means of aeration process and after that the water is saturated with oxygen.

It must be mentioned that eq 10 - 12 ilustrate only the final reactions in the bed, but effective processes are more complicated. These assumptions were useful for the calculation of ion and mass balances in order to estimate the characteristic process indices. Such assumptions were correct, because the calculations were made for all volumes of the bed. Obviously that precise mechanism of the processes in difunctional bed should be explained and it is neccessary for optimizing utilization's total capacity of ion exchanger.

CONCLUSIONS

Difunctional bed with sulphite and hydroxyl forms gave the high efficiency of oxygen and anions removal from the acid solutions. It may be used in the process of water demineralization by the ion exchanger methods.

That bed in concjuction with decationizing of water on strong acid cation exchanger gave high deoxygenation and demineralization of the natural water from the deep well.

Degrees of demineralizing and deoxygenation of water are similar as they may be obtained in the standard processes with the water treatment in higher parameters of its application (for instance as a boiler supply water).

Application of difunctional bed will cause simplification of the water treatment systems using ion exchangers, because in the anion removal step by strong basic anion exchanger, oxygen may be also removed.

The difunctional bed may be very useful when the water must be deoxygenated without thermical processes then "cold process" must be applied.

The efficiency of water demineralizing with the bed is the same such one can obtain using the conventional ion exchanger's method. Simultaneous removal of oxygen from water will cause the elimination of its corrosivity properties.

It may be concluded that the proposed method of the water treatment might be characterized with good operation parameters if the mechanism of processes could be better know.

Author patented the method of simultaneous demineralization and deoxygenation of natural water with using that bed [12].

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