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Journal of Chemical and Pharmaceutical Research, 2013, 5(11):811-817

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Determination of thermal degradation rate of macroporous type Ⅰ anion exchange resin in air-cooled condenser

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ABSTRACT

This paper concerns anion resins used for purification in air-cooled condenser which are subject to thermal-induced degradation. To study the degradation rate of the process, resin samples were submitted to service conditions (50 to 80°C) in pure water. The degradation rate constants were obtained by measuring the strong base exchange capacity. It discussed the factor water-resin ratio (soak solution and resin quality ratio) affecting the thermal degradation rate. It showed that the rate constants obeyed the Arrhenius principle, and the degradation reaction follows zero-order kinetics well. Strong-base exchange capacity loss rate increases with the rising water-resin ratio. This study indicated thermal resistance of anion resin is significantly affected by temperature and quantity of water which may induce the errors in comparison of experimental results and the actual operation condition.

Key words: Air-cooled condenser; Strong base anion resin; Thermal resistance; Degradation

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INTRODUCTION

Ion exchange resins are used in many industrial applications involving purification and separations. One specific application is the purification of condensate water in air-cooled condenser. The temperature of condensate from water-cooled condensers is usually between 5 and 50°C. Air-cooled condensers give higher condensate temperature (40-80°C). The strong base exchange capacity (strong basic groups) of the Type Ⅰ anion exchange resin degradation occurs observably above 60°C. Thermal stability of anion exchange resin is generally the limiting factor for operation temperature of a condenser. High temperature enhances the decomposition of the strong basic quaternary ammonium groups (active sites of anion exchange) to the tertiary amine. Operation at high temperature results in decrease of the capacity of the anion exchange resin.

Published information on the Hoffmann mechanism of the degradation of quaternary ammonium groups of Type Ⅰ anion resin is reasonably enlightened, but thermal degradation reaction kinetic data are controversial. McGarvey [1-3], Baumann [4] and Simon [5] indicated that first-order reactions can explain the degradation rule, and they calculated the half-life of Type Ⅰ anion exchange resin in different temperatures. Russian scholar Tulupov [6] indicated that the degradation of strong base followed second-order kinetics in ethanol and first-order kinetics in water.

Degradation figures [1, 4, 6] show a phenomenon that there is a sharp initial decomposition then the degradation rate became low and stable in the long term stage. The reasons were predicted and discussed [1, 6]. So the description of kinetics of first-order rate reaction is unsatisfactory to the total process of degradation.

In the literature, resin degradation data is scarce under conditions similar to service: high purity water, and service temperatures. Many experiments were conducted at very high temperatures, for example, 70-100°C [1], 100°C [4], 77-121°C [5], 125-150°C [6].

But dynamics analysis of high temperature range limited only 2 or 3 temperature cannot be extrapolated well beyond the experimental temperature to other relatively lower temperatures kinetics. For example, in the literature [1], the values for half lives at lower temperatures (20-50°C) extrapolated by data collected at 70 and 90°C may be subject to substantial errors.

Moreover it has been found that due to different experimental conditions, such as the different water-filter ratio (the water and resin quantity ratio), for the same type resin, the half life determined by first-order kinetics (Table 1) is largely different. The water-filter ratio are separately 2:1, 4:3, 1:1, 10:1 by LiuWeiwei [8], GuoMuying [9], LiuYingchun [10,11], LiangYongjiang [12]. But other studies are lack of description of the test conditions.

Table 1 Different half-life of the anion resin in the literature

	Literature											
	[1]	[3]	[6]	[7]	[8]	[9]	[10]	[11]	[12]	[13]	[14]	[15]
T(℃)	$t_{1/2}$(day)											
70	468	1287	954		40.5~66.6	511				990	500	360
90	43.8	144							35.7~50		72	
95				20.7								
100	14.6		298.8				15.8	21		90	39	

The aim of this work was to study degradation rate at temperatures close or representative of service conditions and analyze the reaction kinetic of degradation.

EXPERIMENTAL SECTION

2.1. Materials

Macroporous Type Ⅰ strong base anion exchange resins consist of a polystyrene backbone, cross-linked with divinylbenzene were used in these experiments. The products were Rohm & Haas Amberlite IRA-900, Baye MP500 and Purolite A500TL, which were provided by the power plants of Zhao-guang, Yu-she and Gu-jiao. For proprietary and commercial reasons, the resins will be coded as ZG, YG and GG.

The resin preparation and conversion techniques were based upon standard methods.[16-18]. After conversion to OH-form, the resin was rinsed with pure water until the effluent pH was near neutral.

2.2 Main experimental conditions

The thermal degradation experiments were conducted with demineralized water that the conductivity (25°C) is below 1μS/cm. The samples dryed external moisture were measured and transferred in a pre-cleaned closed glass column and attached to demineralized water. With a certain water-resin ratio, it was heated in water bath.

In order to study the thermal resistance of the resin under service conditions, the data of condensate water temperature were collected in three air-cooled power plants including Matimba [9], China Inner Mongolia [19] and China Shanxi (Table 2).

Table 2 The accumulation time of the condensate water temperature by a power plant in China Shanxi

	Month	June		July		August		September		Total	
T/°C		#3	#4	#3	#4	#3	#4	#3	#4	#3	#4
>75	t/h	0	0	4.5	0	0	0	0	0	4.5	0
70-75		1.5	1.5	60	25.5	0	1.5	0	1.5	61.5	30
60-70		111	82.5	336	157.5	129	66	190.5	90	766.5	396
50-60		280.5	274.5	241.5	285	313.5	283.5	520.5	460.5	1356	1303.5
<50		321	363	78	249	279	369	709.5	862.5	1387.5	1843.5

According to this, The experimental temperature range (50-80°C) and accumulation time is set (Table 3). Test time is more than service time in 70-80°C for study.

Table 3 New resin thermal resistance experiments

T/°C	50	55	60	65	70	75	80
t/h	576	576	480	288	288	288	264

2.3 Temperature effect on heat-resistant experiment

Firstly, according to standard [17], the strong base exchange capacity (Q_0) of resin samples before heat would be determined. After every 48hrs, 0.5000g resin was removed out, and the strong base exchange capacity at time *t* (Q_t) and residual exchange capacity ratio *P* ($P=Q_t/Q_0$) would be measured and calculated.

The curve of *P*-*t* would be plotted and the formula would be fitted for the degradation rate constant (*k*). The logarithmic of degradation rate constant (*ln*k) plotted against the reciprocal of the Kelvin temperature (1/T) can be analyzed for Arrhenius relationship.

2.4 Effect of water-resin ratio experiment

We set different water-resin ratios (N) respectively in 1, 5, 20, 100, 500 and 1000 and studied the effect on the heat-resistance of YG resin in 70°C for 96hrs. The strong base exchange capacity (Q_t) before and after heat would be determined of drawing the Q_t -N curve.

RESULTS AND DISCUSSION

3.1 Effects of temperature

3.1.1 Degradation results

In Fig. 1 to Fig. 7, it can be seem the curves of the residual capacity ratio of resins (*P*) with time *t* at high temperature. The dotted line represents the connecting line of the measured point. The solid line shows the fitted line for the stable degradation stage.

Heat-resistance of resins is different. Fig. 7 shows that, the heat-resistance of YG with poor stability compared with GG and ZG.. From Fig. 1 to Fig. 6, the degradation rate of YG was increasing with the rising temperature at 50-80°C. ZG and GG were relatively stable at 50-55°C, but as the temperature above 60°C, the strong base deceased obviously with heating time.

Fig. 1, Fig. 3 and Fig. 5 showed the thermal resistance of resins in the water-resin ratio of 200:2. Initial degradation rate of YG with poor stability is rapid at low temperature (50-55°C) ; initial sharp degradation of ZG and GG are at higher temperature (60-65°C). As temperature beyond this stage, this phenomenon disappears. Degradation rate increased significantly due to the rising high temperature, which can conceal the effect of large water-resin ratio on the degradation rate.

Moreover when the water-resin ratio is decreased, like small water-resin ratio of 200:6, the strong base deceased always with linear relationship and did not appear the first quick decreasing phenomenon. Degradation rate was quickly in the initial short period and then the strong base degraded slowly with linear relationship. The degradation rate was represented by a constant *k*, which was the slope of the fitting line of *P* and *t* in the stable period. The *k* rise with the temperature increasing. And in static experiment, the greater the water-resin ratio was, the larger the *k* would be.

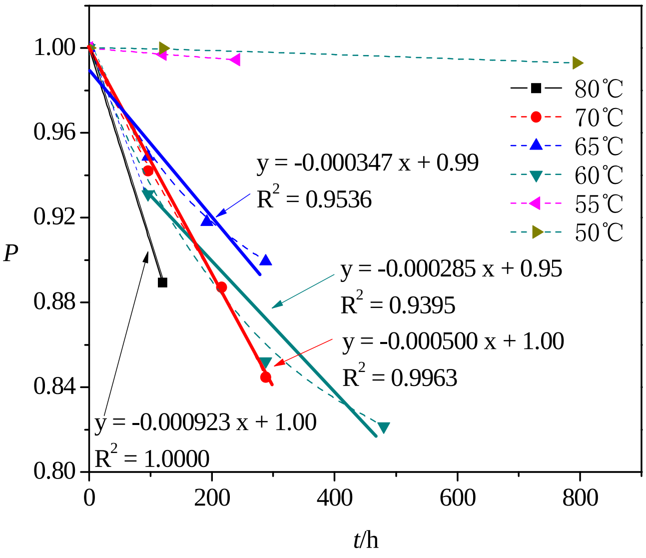

Fig. 1 The relationship between fraction of strong base exchange capacity of ZG and heating time at different temperature (N=200:2)

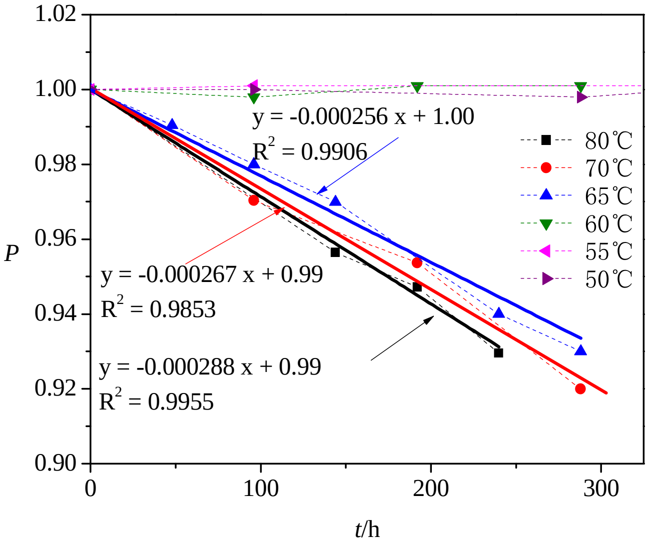

Fig. 2 The relationship between fraction of strong base exchange capacity of ZG and heating time at different temperature (N=200:6)

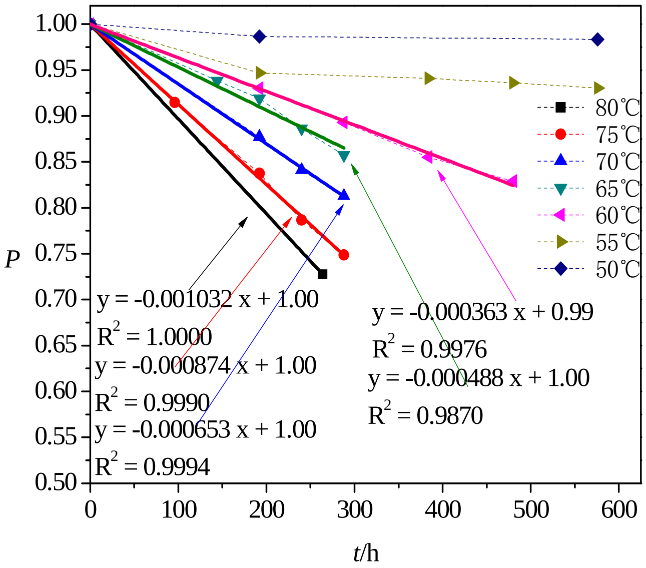

Fig. 3 The relationship between fraction of strong base exchange capacity of YG and heating time at different temperature (N=200:2)

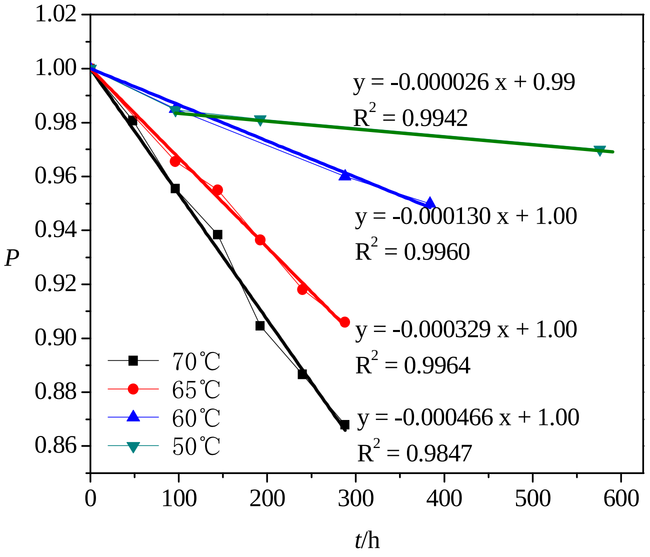

Fig. 4 The relationship between fraction of strong base exchange capacity of YG and heating time at different temperature (N=200:6)

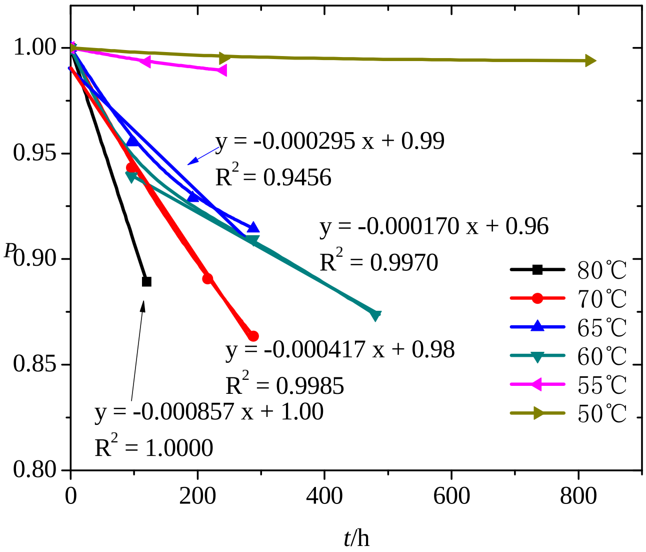

Fig. 5 The relationship between fraction of strong base exchange capacity of GG and heating time at different temperature (N=200:2)

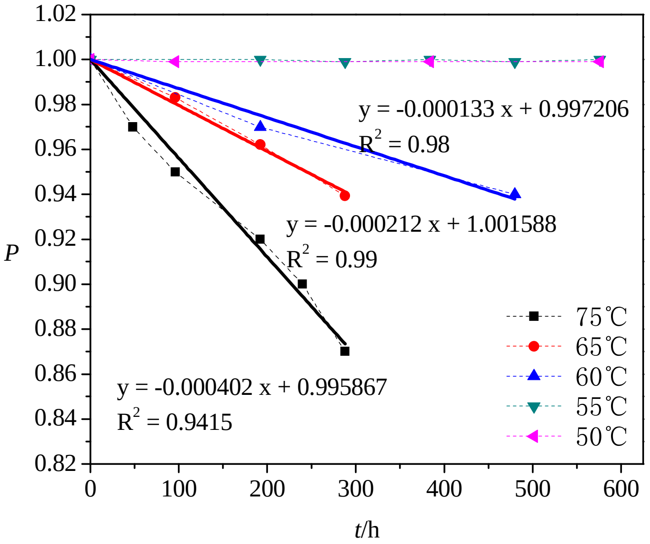

Fig. 6 The relationship between fraction of strong base exchange capacity of GG and heating time at different temperature (N=200:6)

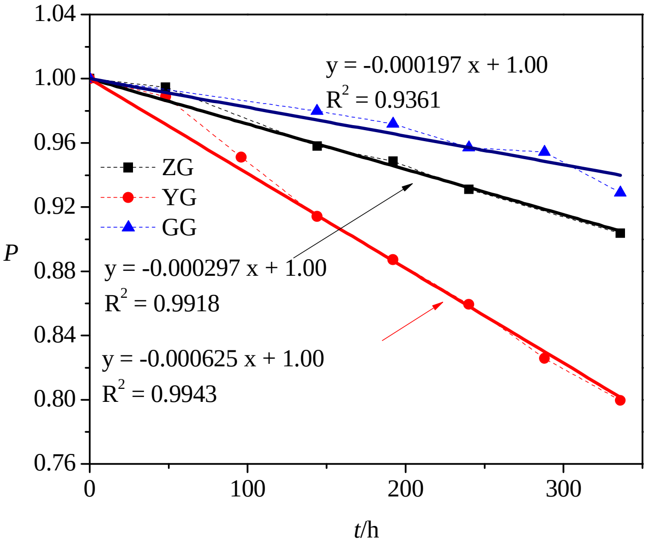

Fig. 7 The relationship between fraction of strong base exchange capacity and heating time at 80℃ (N=200:25)

3.1.2 Kinetics Analysis of degradation

Under stable degradation stage, residual ratio of strong base (*P*) and the heating time *t* has a linear relationship. The logarithmic of degradation rate constant (*lnk*) and the reciprocal of the Kelvin temperature (*1/T*) were plotted and fitted by formula, as shown in Fig. 8 to Fig. 10. The *k* and *1/T* meet the Arrhenius equation: $k=A\exp(-E/RT)$, i.e. *lnk* and *1/T* should meet a linear relationship, *E* is the activation energy. It is inferred that the strong base degradation reaction follows zero-order kinetics range from 60 to 80°C. And as N ≤ 200:6, it is able to better follow zero order reaction kinetics.

According to zero-order reaction kinetics equation, the half-life (unit: month) of *P* can be calculated by $t_{1/2} = \dfrac{0.5}{k\cdot 24\cdot 30}$ to predict the resin life.

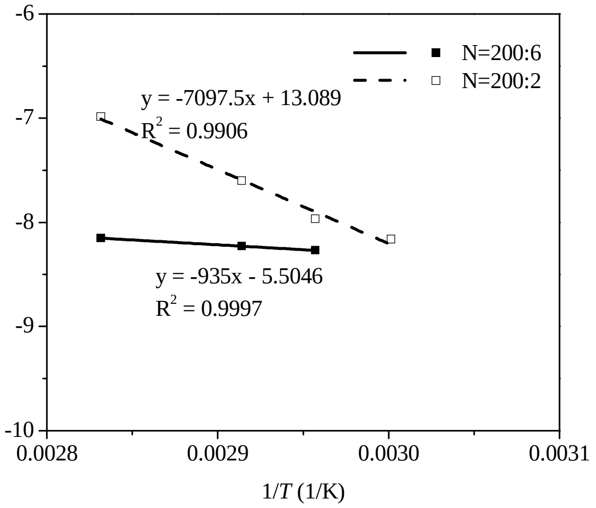

Fig. 8 Arrhenius plots of the loss of strong base exchange capacity of ZG

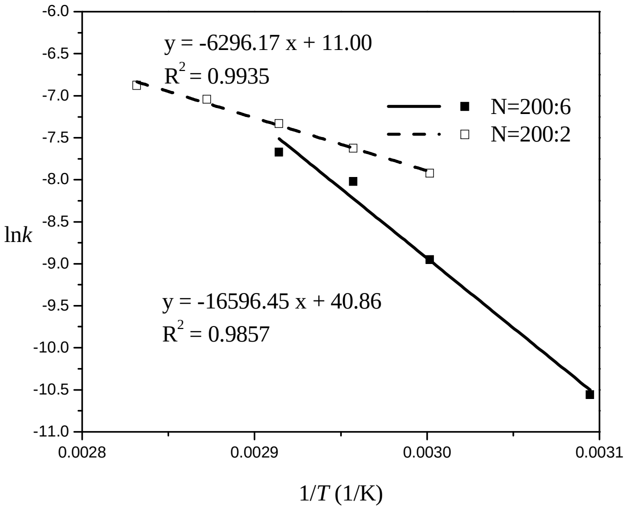

Fig. 9 Arrhenius plots of the loss of strong base exchange capacity of YG

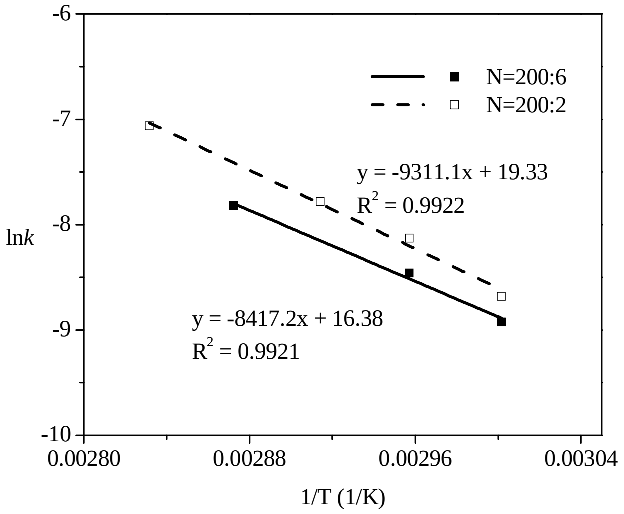

Fig. 10 Arrhenius plots of the loss of strong base exchange capacity of GG

3.2 Effect of water-filter ratio

Before experiment, the strong base exchange capacity (Q_0) was 1.23mmol/g. After heat at 70°C for 96hrs, *Q* was determined, *Q* and the water-resin ratio were plotted, as shown in Fig. 11.

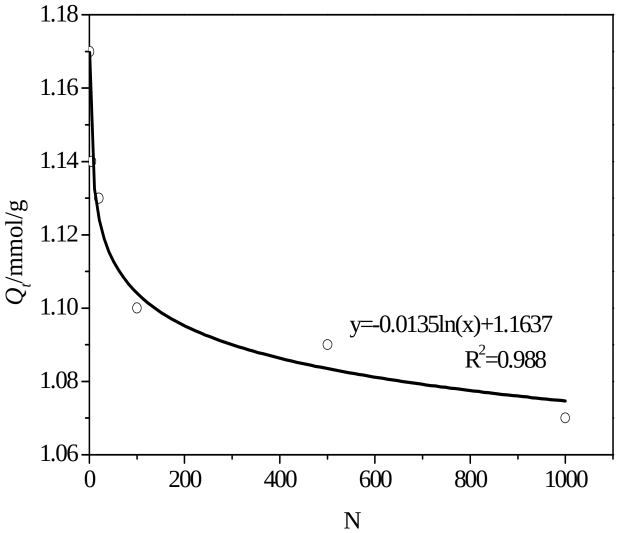

Fig. 11 The relationship between remaining strong base exchange capacity and water-resin ratio of YG

From Fig. 11, it can be found that *Q* declined at a logarithmic relationship with the increase of water-filter ratio. The reason of the effect may be in static experimental conditions, when the water-resin ratio is small, the high concentration degradation reaction product in the water restrained the degradation reaction. On the contrary, large water-filter ratio will promote the degradation reaction balance forward.

Another reason may be a large number of low molecular weight polymers in new resin can be dissolved by pure water, which has the solubilizing effect to the resin matrix. Large water-filter ratio promote the diffusing rate of oligomers, at the same time the solubilizing effect at high temperatures will induce and exacerbate the skeleton degradation.

CONCLUSION

Heat-resistance is different with different resins. The anion resin degradation rate increases with the rising temperature and are significantly in the range of 60-80°C. Degradation reaction follows zero order reaction kinetics. When water-resin ratio is low (N≤200:6), the degradation rate is a fixed value at constant temperature. The effect of water-resin ratio is greatly on the anion resin degradation rate. The increasing water-resin ratio will significantly promote the degradation of alkaline groups of resin. To study on degradation dynamics, the value of water-resin ratio must be fixed. Otherwise the results under different water-resin ratio are not comparable.

There are many factors affecting the static experiment, the errors are still large in comparison of experimental results and the actual operation data. Further research is needed on the various factors affecting the static immersion heating experiment. Moreover improve the experiment conditions to make it more close to the actual production conditions.

REFERENCES

[1]Shao, L. Water treatment ion exchange resin, 1st Edition, Water Power Press: Beijing; **1989**, 169-171.
[2]F. X. McGarvey & Co. Field Experience with the Stability of Strong Base Resin at Corpus Christi Petrochemical Company, In 47th. Inter. Water Conf., proceedings of the international water conference, October 27-29, **1986** Pennsylvania, U.S.A. Michael C. Skriba, Eds.; Pittsburgh, **1986**.
[3]F. X. McGarvey & Co. Thermal Degradation of Strongly Basic Anion Exchange Resins in Caustic Regenerants, In 48th. Inter. Water Conf., proceedings of the international water conference, Nov. 2-4, 1987 Pennsylvania, U.S.A. E. Peter Benzing, Eds.; Pittsburgh, **1987**.
[4]E. W. Bauman. *Academic J. Chem. Eng. Data*, **1960**, 5, 376.
[5]G. P. Simon. The Thermal Degradation of Hydroxyl Form Strong Base Type I Anion Exchange Material In 47th. Inter. Water Conf., proceedings of the international water conference, October 27-29, **1986** Pennsylvania, U.S.A. Michael C. Skriba, Eds.; Pittsburgh, **1986**.
[6]P. E. Tulupov P E; N. G. Polyanskii N G. *Academic J. Russian chemical reviews*, **1973**, 9, 754.
[7]Zhang Chengxin, Qian Qin, Li Qin et al. Guide for selecting ion exchange resins used in water treatment of thermal power plant. CN Standard DL/T 771-**2001**, **2002**-02-01.
[8]Liu Weiwei. Study on the resin heat resistance performance of air-cooling unit condensate polishing treatment. Published dissertation. Baoding, North China Electric Power University, **2011**

[9]Guo Muying. *Academic J. Ion Exchange and Adsorption*, **1994**, 3, 258-263..
[10] Liu Yingchun. synthesis thermal stabilities and applications of stronge base anion exchange resin with alkylene space chains. Published dissertation. Jiangsu Polytechnic University, **2009**
[11] Chen Qun, Liu Yinchun, Sun Qi etal. *Academic J. Journal of Molecular Catalysis*, **2009**, (03), 243-247
[12] Liang Yongjiang. screening and optimizing of nuclear grade resin in tqnpc. Published dissertation. Shanghai, Shanghai Jiaotong University, **2007**
[13] Fan Yunge, Xiao Guolin. *Academic J. Ion Exchange and Adsorption*, **2000**, 4, 4.
[14] Phillip J. D'ANGELO & Co. Operation of powdered resin units at high temperature// , In 63rd. Inter. Water Conf., proceedings of the international water conference, Oct. 20-24, 2002 Pennsylvania, U.S.A. Fred Potthoff, Eds.; Pittsburgh, **2002**.
[15] Liu Fenfen, Sun Haijun, Xu Hongtao et al. *Academic J. Water Purification Technology*, **2009**, 6, 65-68.
[16] Zhang Yingzu, Yu Rong, Zhang Wenyan Methods for pretreating ion exchange resins. CN Standard GB/T 5476-1996, **1997**-05-01.
[17] Shao Lin, Wang Guangzhu, Cui Huanfang et al. Determination for exchange capacity of anion exchange resins in hydroxyllic form. CN Standard GB/T 5760-**2000**, **2000**-09-01.
[18] ASTM, Test Methods for Physical and Chemical Properties of Particulate Ion-Exchange Resins, American Society for Testing and Materials, ASTM Book of Methods, D2197-94, **1998**.
[19] Yang Kai, Wang Yuehe, Zhang Xuefei et al. *Academic J. Inner Mongolia Electric Power*. **2007**, 33(6), 25-27.